

Overview of CWRU Work on Metallic Glasses and Advanced/Additive Manufacturing



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Outline

- **Overview of Glasses/Bulk Metallic Glasses**
- **Quasi-Static Flow Behavior**
 - **Stress State Effects on Flow Behavior at $T \ll T_g$**
 - **Stress State Effects on Flow Behavior at $T \approx T_g$**
- **Quasi-Static Fracture Behavior**
 - **Fracture Behavior/Damage Tolerance**
 - **Notch/Fracture Toughness**
 - **Effects of Chemistry Changes/Annealing-Induced Embrittlement**
 - **Correlation with Elastic Constants**
 - **Alloy Design - Fe-based BMG, Ti-based BMG**
 - **Toughening Approaches**
- **Creation of Micro/Nano Metallic Glass Wires**
 - **Review of Recent Techniques**
 - **Initial Testing of Micro/Nano Wires**
 - **Effects of Sample Size and Preparation on Plasticity**
- **Advanced/Additive Manufacturing**



Acknowledgements

Materials:

J. Poon – University of Virginia	(Fe, Ti based, Ni-Ta-X)
W.L. Johnson – Cal Tech	(Zr based bulk & composite)
J. Kajuch/A. Peker – Liquidmetal	(Zr based)
T. G. Nieh – LLNL/U Tenn	(Cu based)
G. Shiflet – University of Virginia	(Al based, Ni-Ta-X)
T. Hufnagel – Johns Hopkins Univ.	(Hf and Zr based)
L. Kecskes – ARL	(Zr based composites)
G. Wolter – Howmet	(Zr based bulk & composites)
W.H. Wang - Chinese Acad. Sciences	(Mg and Ce based)
A.L. Greer - Cambridge University	(Zr based)
M. Widom – CMU	(Ni-Ta-X)

Students/Collaborators:

P. Lowhaphandu	L. Vatamanu
J. Caris	H. Hassan
P. Wesseling	F. Yuan
A. Thurston	B. Ko
A. Shamimi Nouri	A. Shabasy
G. Sunny	C. Tuma
A. Awadallah	V. Prakash
N. Stelmashenko	A. Vormelker
L. Deibler	L. Kecskes
M. Seifi	J. Carter
J. Booth	N. Neilson

Interactions:

ARL	Univ. Cambridge
Boeing	Tohoku Univ.
Pratt & Whitney	CWRU
Liquidmetal	DARPA/DoE
SRI	ONR
CAL TECH	ARO
Univ. Virginia	Chinese Acad. Sci.



Melt-Spinning

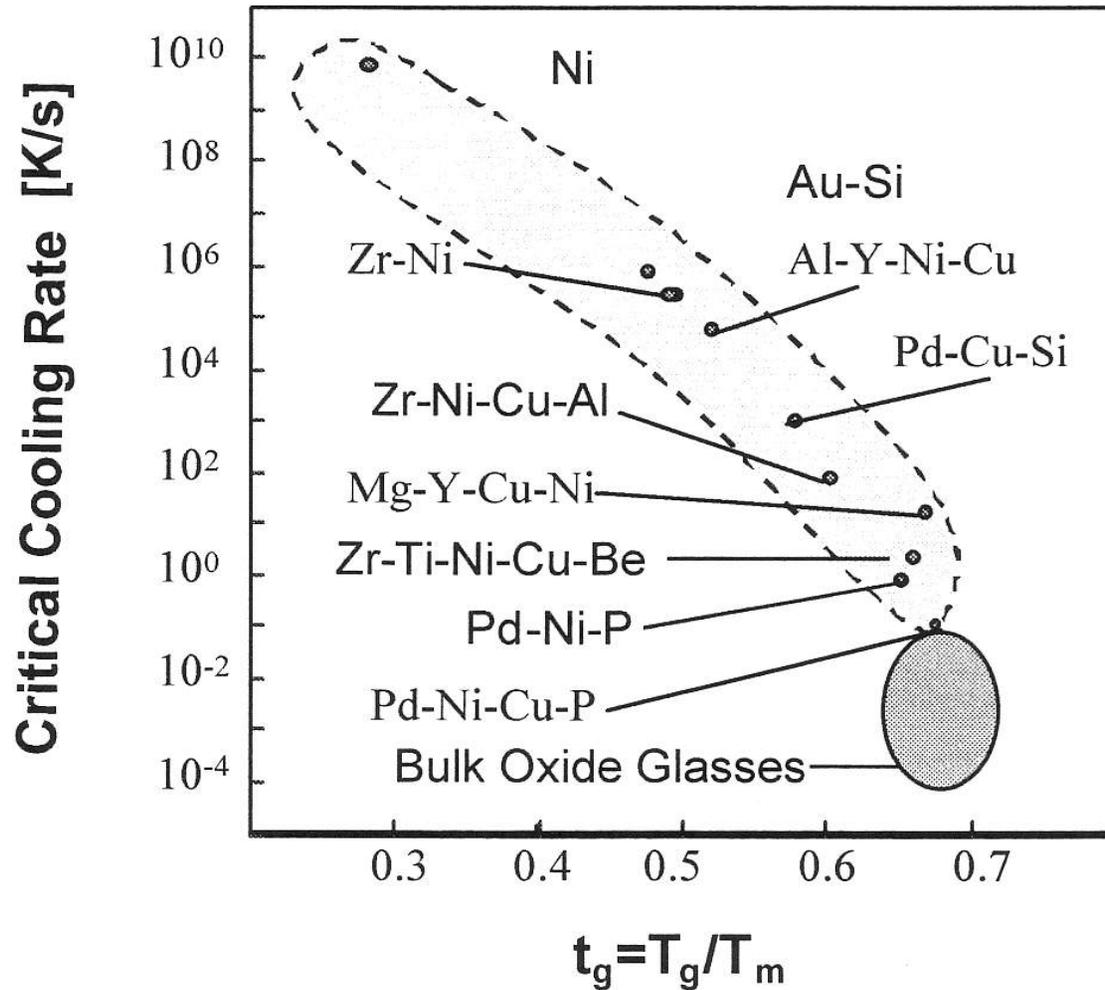
Ribbon Thickness $< 100 \mu\text{m}$, Ribbon Width mm - 10' s mm

Can be Devitrified to Produce Nano-crystalline solid

Mechanical Testing Limited: Tension, Bend Testing, Hardness (Alignment Issues)



Increase in t_g (Reduced Glass Transition Temperature) Lowers the Critical Cooling Rate to Produce Bulk Metallic Glasses



Guidelines:

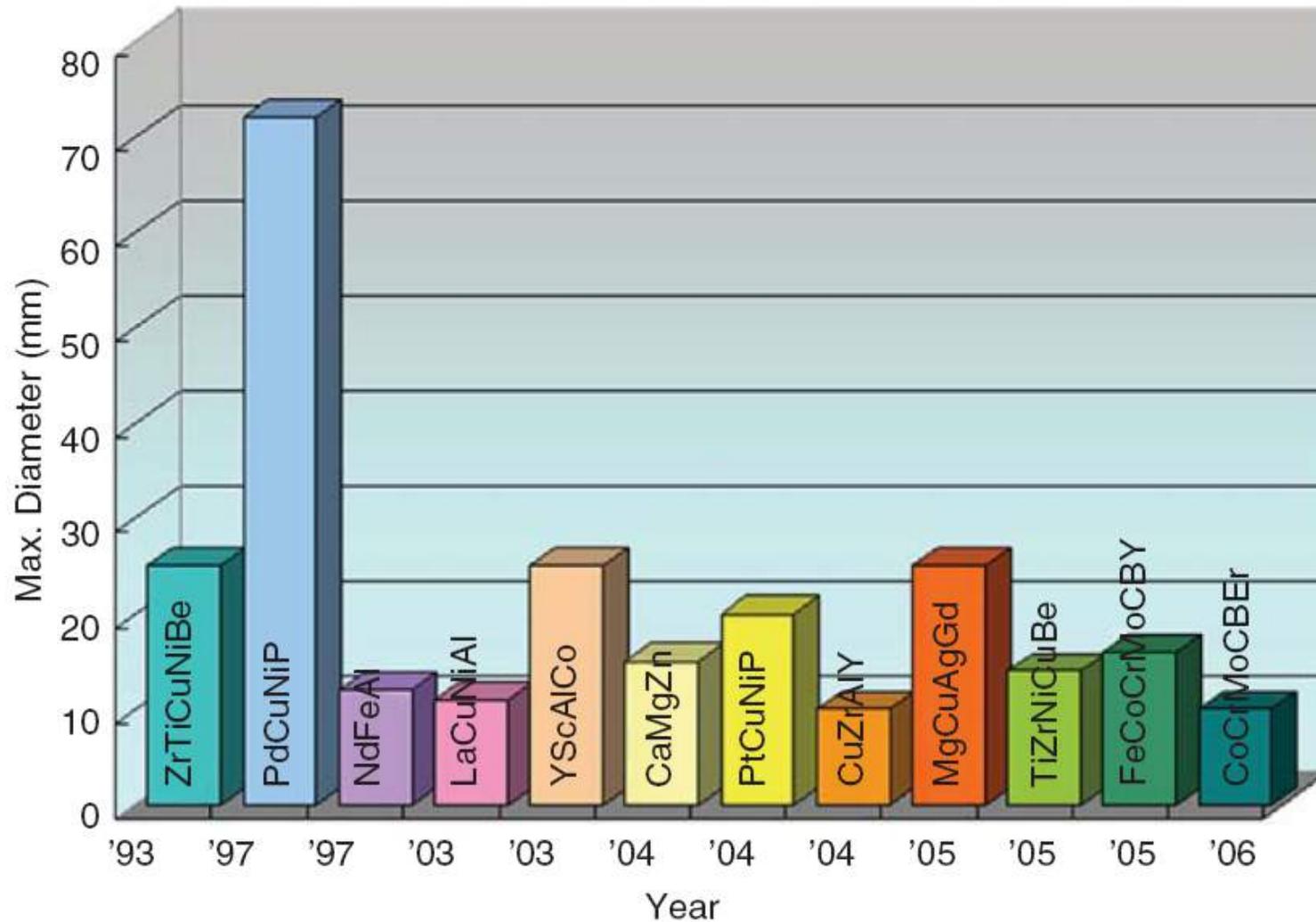
- Typically > 3 Elements
- Difference Atom Sizes > 12%
- Negative Heats of Mixing
- Deep Eutectic
- Dense Random Packing (small excess free volume 1%) (No Long Range Order) (MRO, SRO exist)

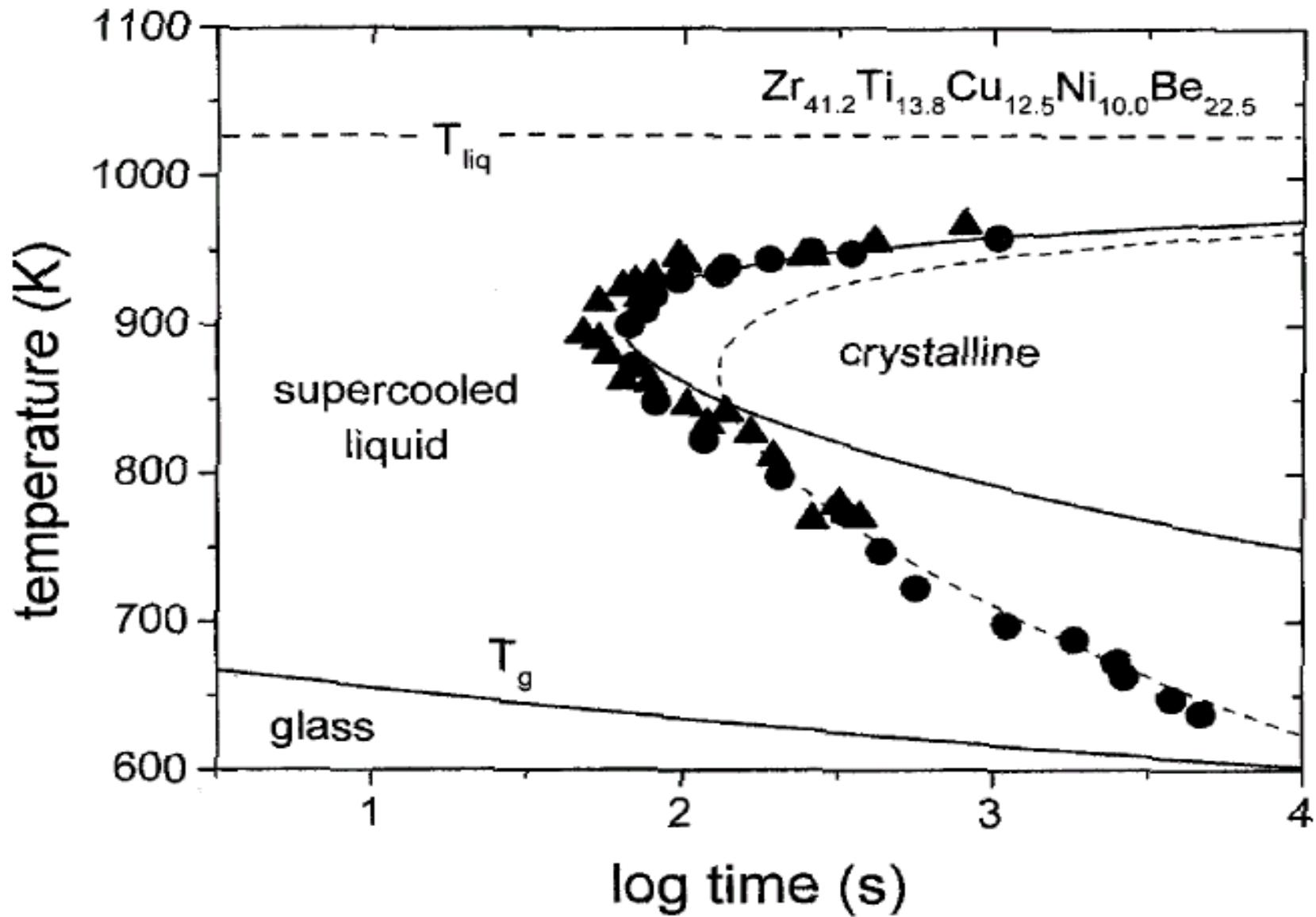


Ref: Peker, A. and Johnson, W.L. Appl. Phys. Lett., vol. 63, 1993, p. 2342.



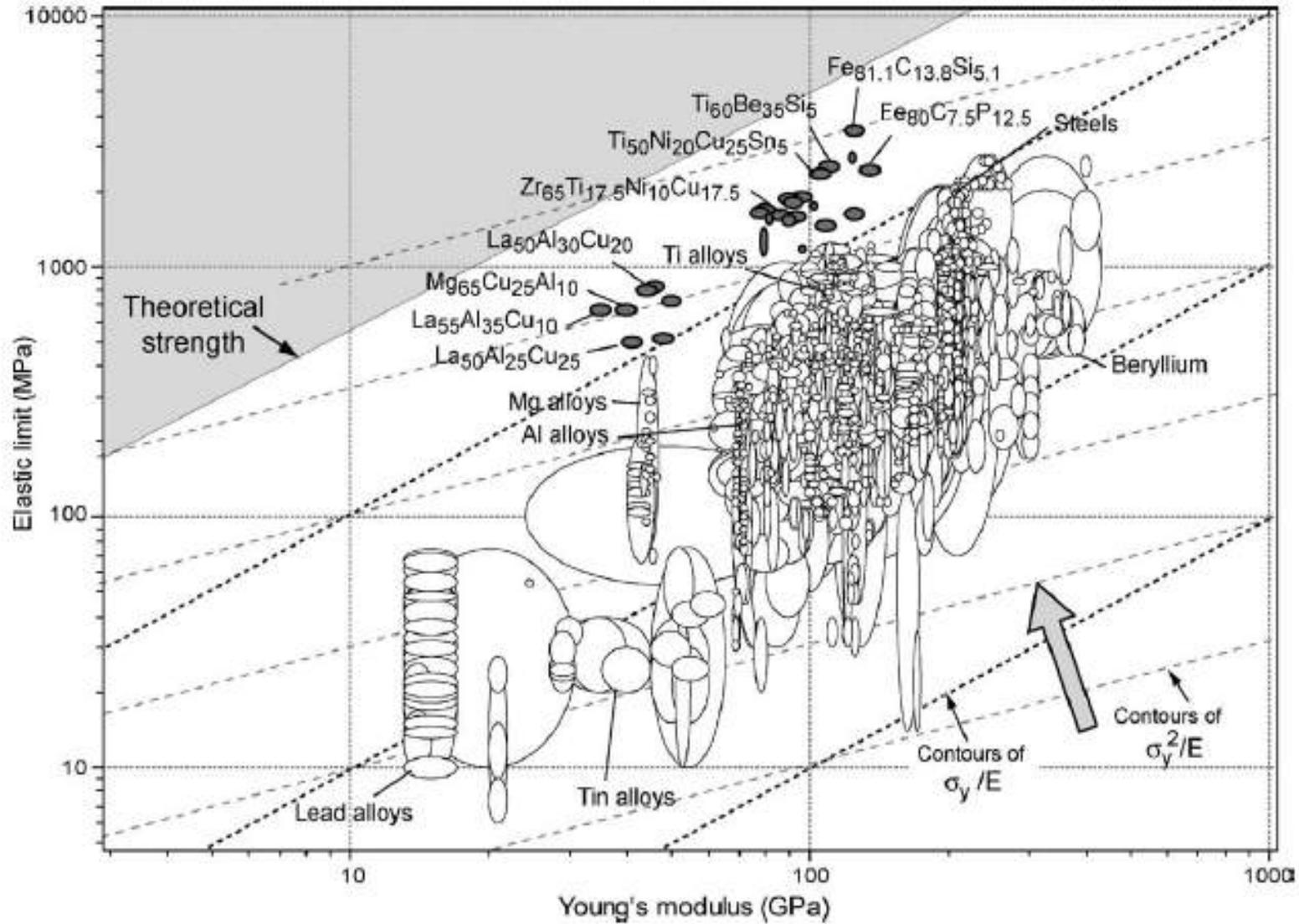
Evolution of Metallic Glass Chemistry and Maximum Sizes





R. Busch, JOM (2000)

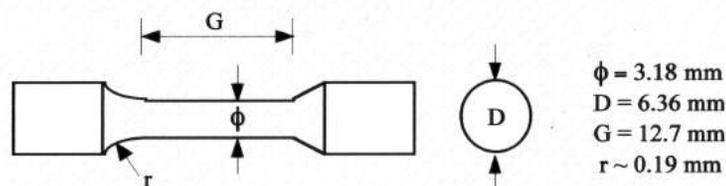




Experimental Methods

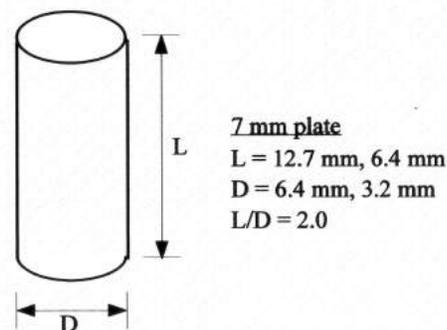
* Tension Testing

- ASTM E8
- Displacement-control; initial strain rate of 10^{-3} sec^{-1}
- High Pressure Deformation Apparatus



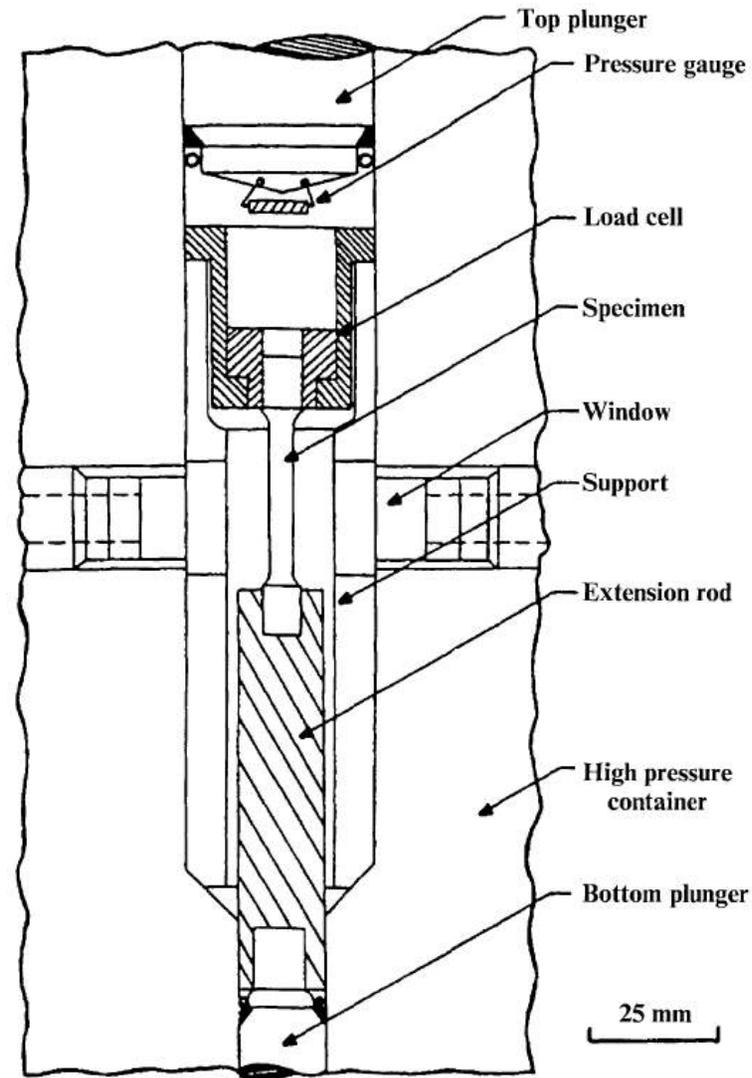
* Compression Testing

- ASTM E9
- Displacement-control, initial strain rate of 10^{-4} sec^{-1}
- 20 kip MTS servohydraulic testing machine



Specimens were polished to a $0.25 \mu\text{m}$ finish.

Superimposed Pressure Testing



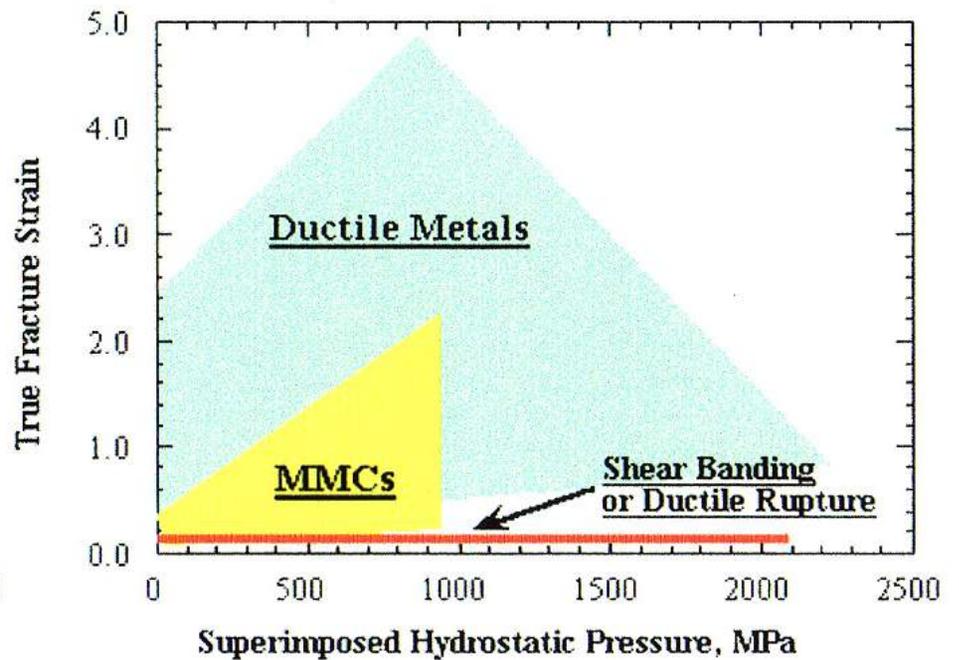
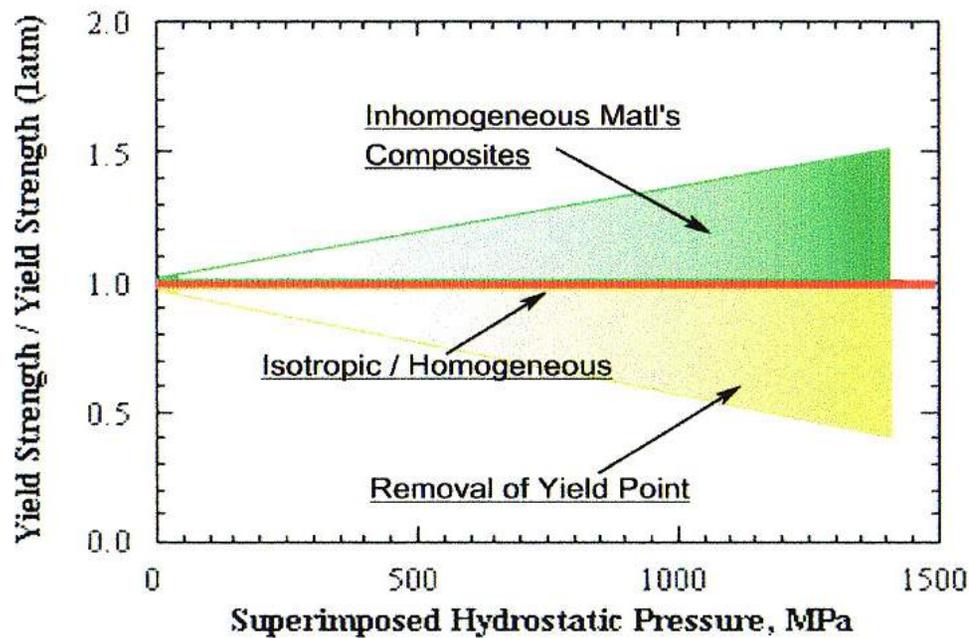
1 Schematic diagram of oil based high pressure deformation apparatus^{36,72,122,126,269,326-329}

J.J. Lewandowski and P. Lowhaphandu, International Materials Reviews, Vol.43, No.4, 1998.

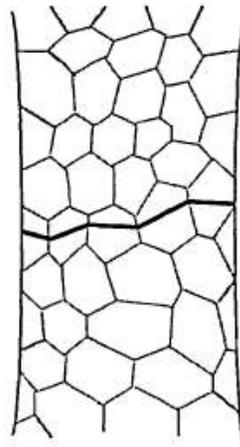
Silicone Oil Rig
Pressure = 2 GPa
Can Heat Oil to 330°C

Previous Work Summary

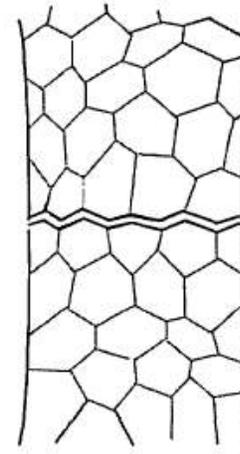
High Pressure Effects on Metals and Metallic Composites



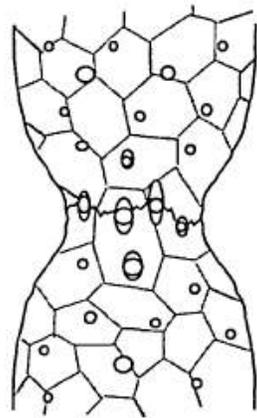

 Loading
 Direction



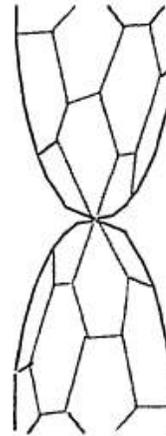
(a)



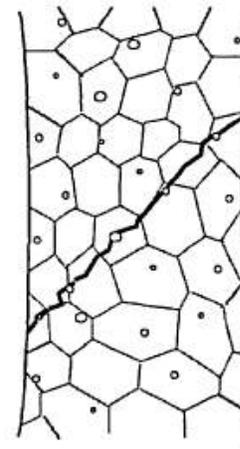
(b)



(c)



(d)

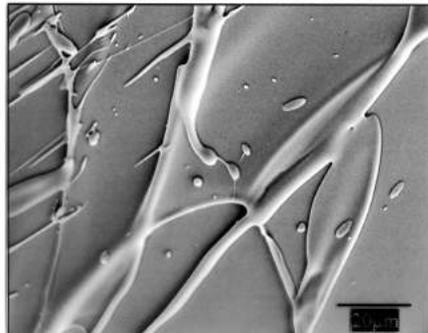
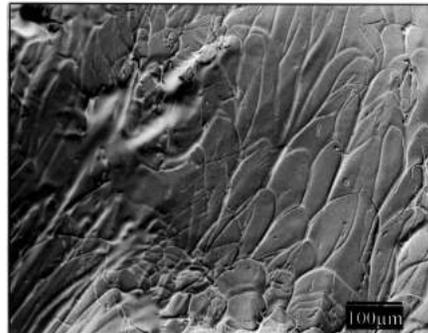
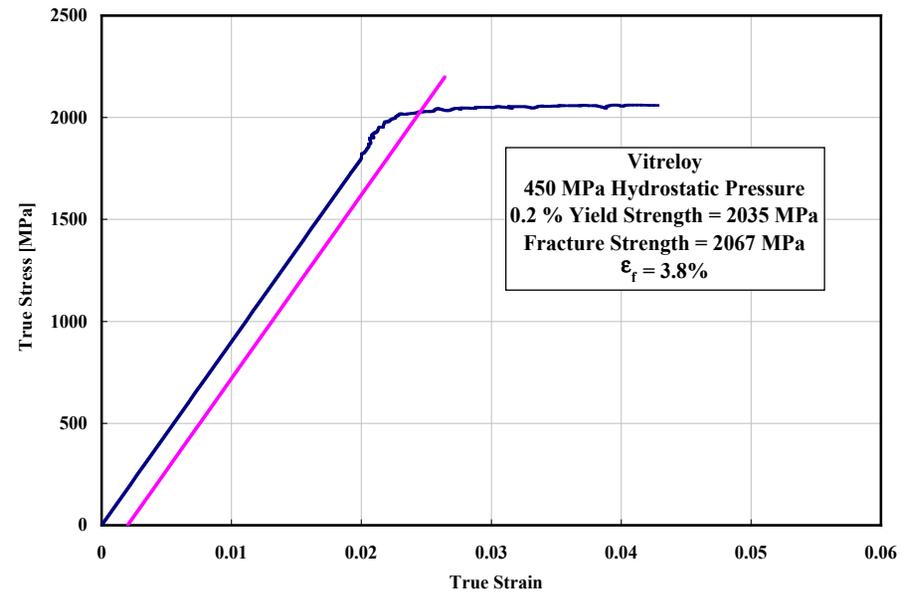
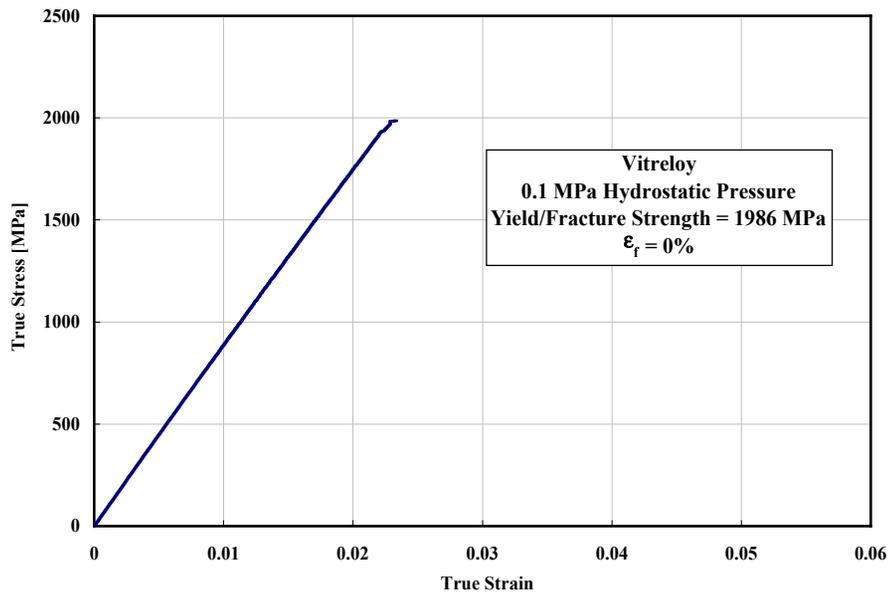


(e)

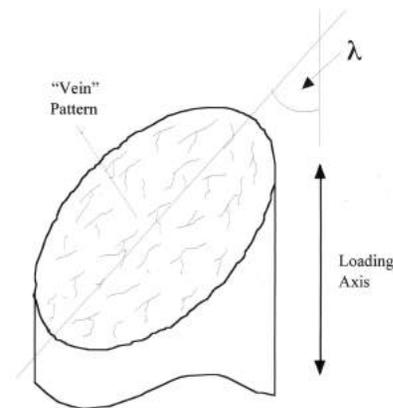
a transgranular cleavage; *b* intergranular fracture; *c* microvoid coalescence or dimpled rupture; *d* ductile rupture; *e* localised shear

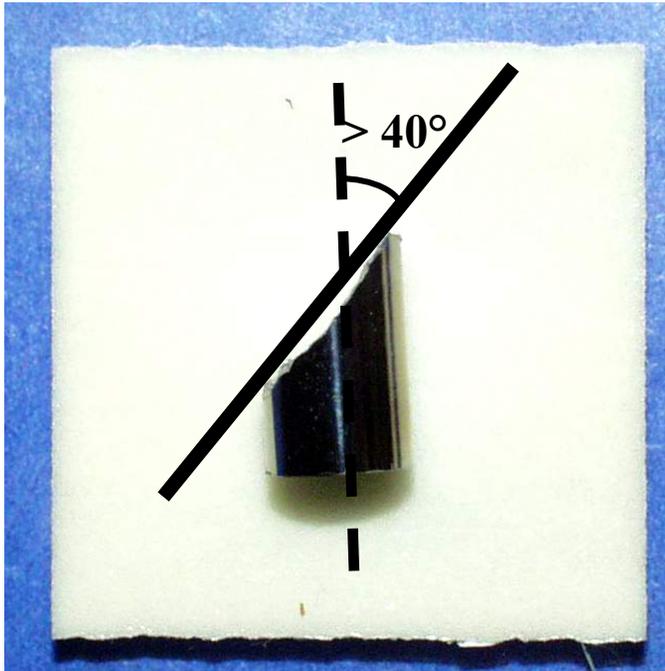
16 General categories of fracture processes in metallic materials^{351,352}

J.J. Lewandowski and P. Lowhaphandu, International Materials Reviews, Vol.43, No.4, 1998.

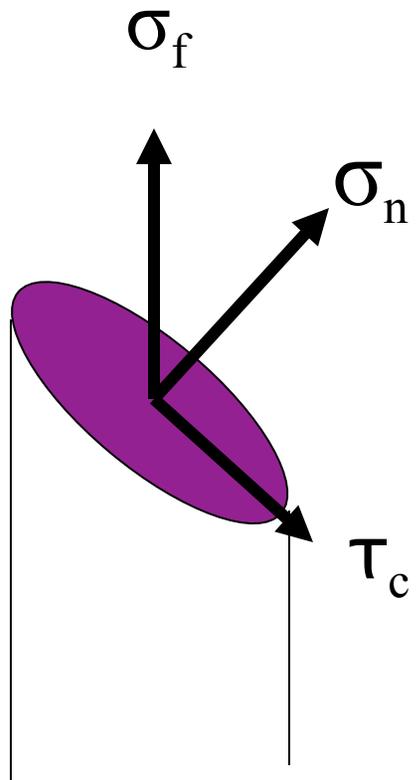


Specimen Fails in Shear





Mohr-Coulomb Criterion



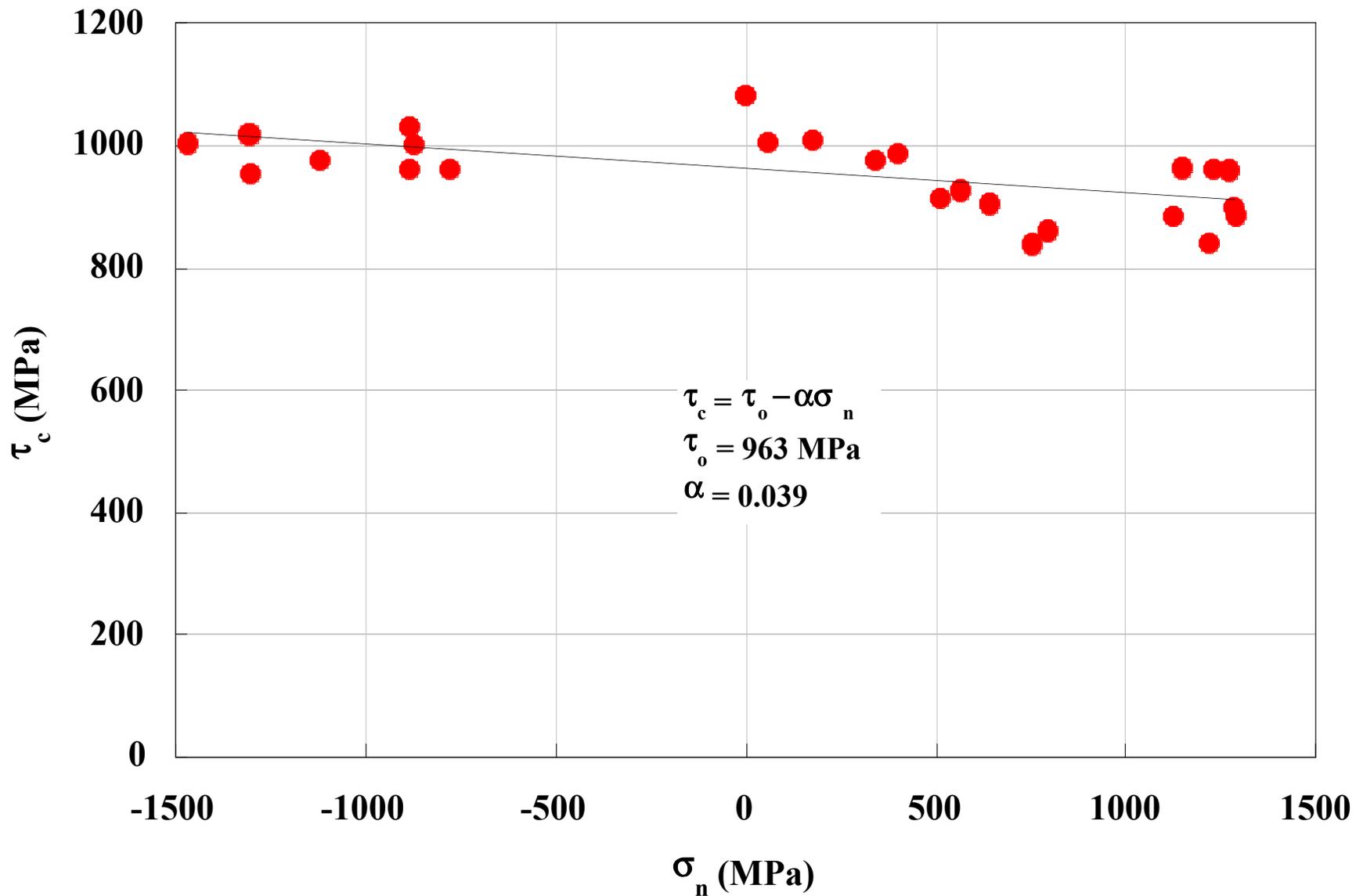
$$\tau_c = \tau_0 - \alpha' \sigma_n$$

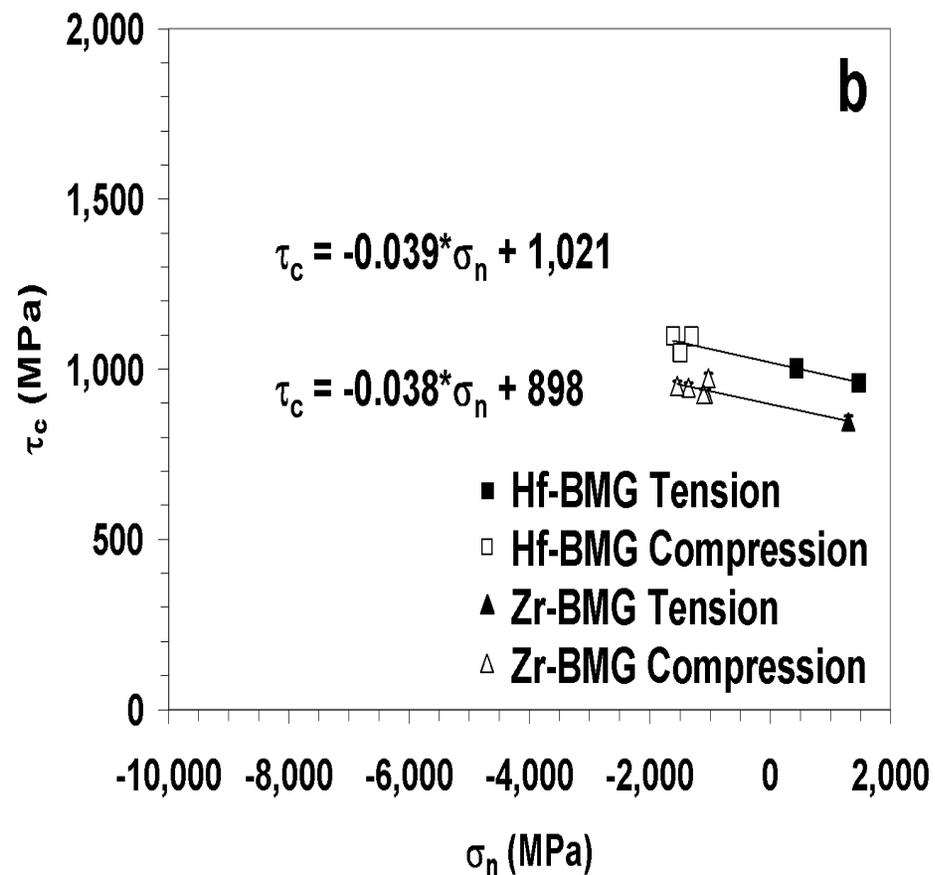
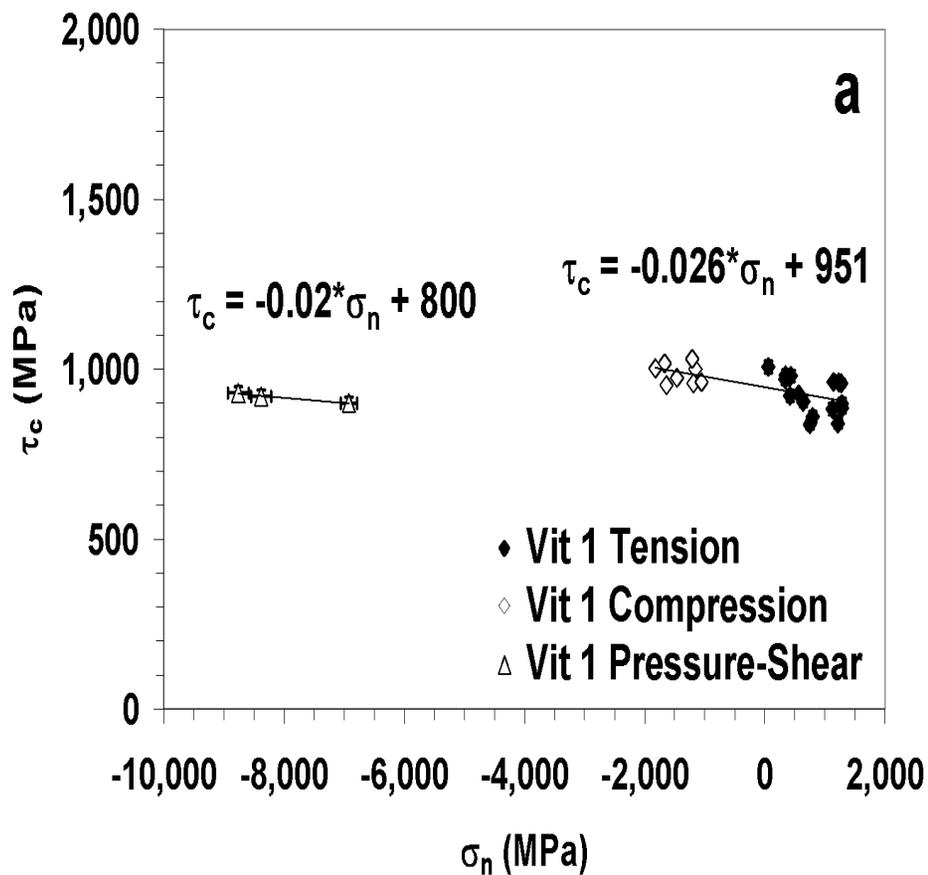
τ_c = critical shear stress

τ_0 = shear stress in torsion

σ_n = normal stress

α' = constant expressing the magnitude of normal stress dependence. □





Caris, J. and Lewandowski, J.
Acta Materialia, Vol. 58, No. 3, Feb. 2010, pp. 126-136.

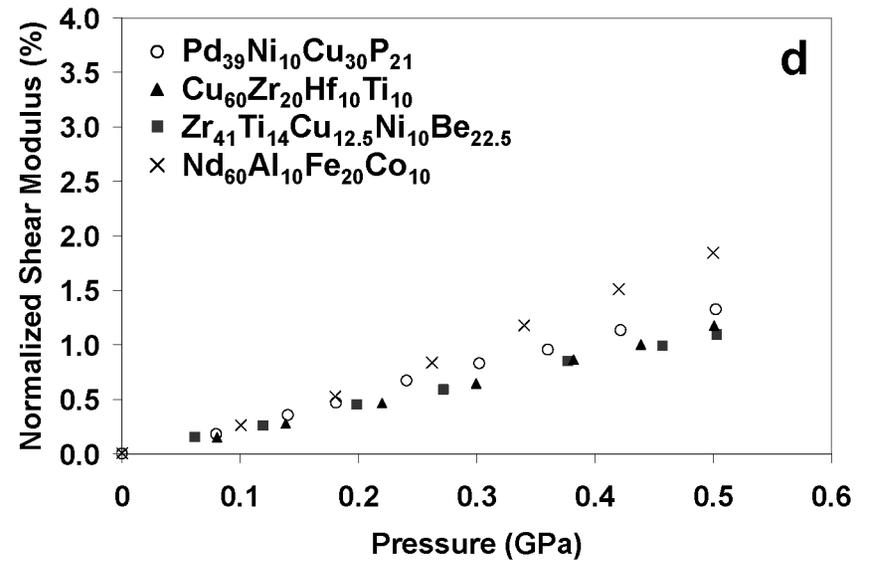
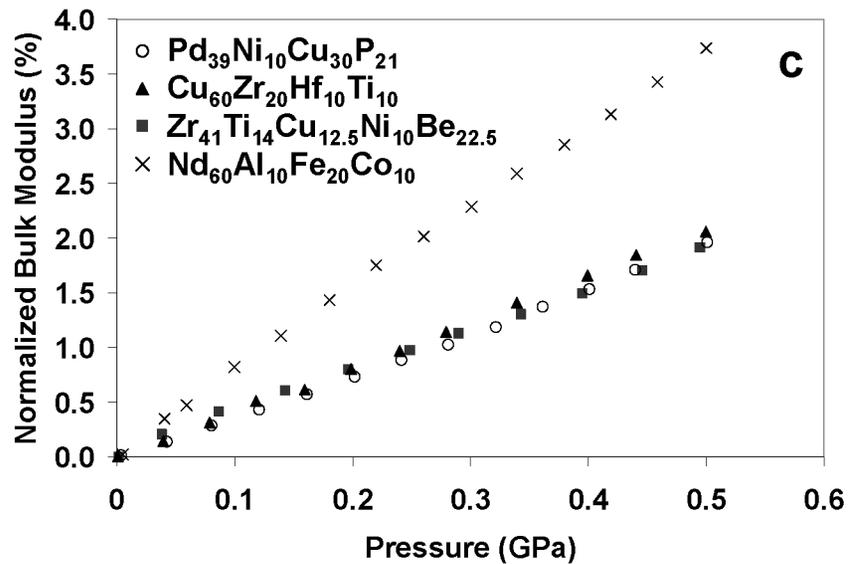
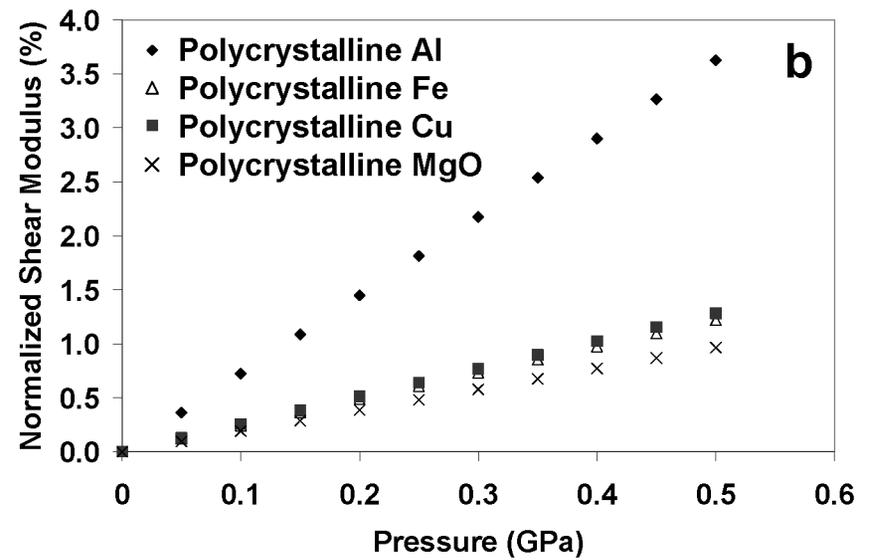
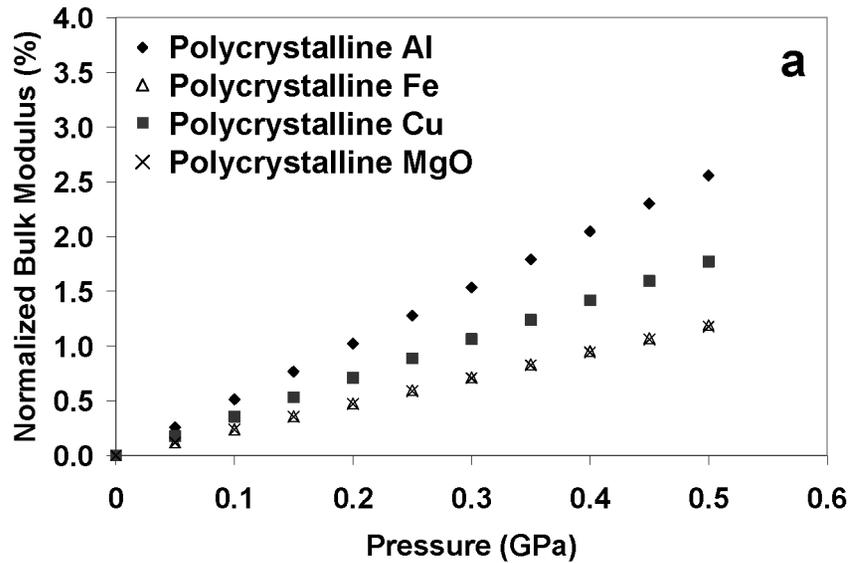


Material	Test	α	k_o (MPa)
Vit 1	Pressure-Shear	0.02 ± 0.01	800 ± 100
Vit 1	Quasi-static	0.026 ± 0.002	951 ± 2
Zr-BMG	Quasi-static	0.038 ± 0.007	898 ± 9
Hf-BMG	Quasi-static	0.039 ± 0.007	1021 ± 9
Sand-cement mortar [32]	Quasi-static	0.573	9.86
Concrete [32]	Quasi-static	0.814	11.54
Granite Rock [32]	Quasi-static	1.455	19.42

Caris, J. and Lewandowski, J.

Acta Materialia, Vol. 58, No. 3, Feb. 2010, pp. 126-136.





Spitzig, WA, Richmond, O. *Acta Mat'l*, 32(3), 1984, 457.

Wang, W.H. et al "EOS of BMGs Via Ultrasonic Method", *APL*, 79(24), 3947, 2001.

Wang, W.H. et al, *Acta Materialia*, 52,715, 2004.



Material	G_o (GPa)	K_o (GPa)	dG/dp	dK/dp	G_o/K_o
Al (polycrystalline) [17]	26.2	76.2	1.9	3.9	0.344
α -Fe (polycrystalline) [17]	90.2	168.0	2.2	4.0	0.537
Cu (polycrystalline) [17]	54.6	138.3	1.4	4.9	0.395
MgO (polycrystalline) [17]	134.6	166.0	2.6	3.9	0.811
Vit1 to 0.5 GPa [18]	39.5	114.1	0.85	4.2	0.346
Vit1 to 2 GPa [19]	37.4	114.1	0.76	4.0	0.328
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ [20]	36.9	128.2	0.87	5.4	0.288
$Nd_{60}Al_{10}Fe_{20}Co_{10}$ [21]	20.7	46.5	0.95	3.4	0.445
$Pd_{39}Ni_{10}Cu_{30}P_{21}$ [22]	35.1	159.2	0.78	6.2	0.220

(17) Spitzig, WA, Richmond, O. *Acta Mat'l*, 32(3), 1984, 457.

Haasen, P., Lawson, AW. *Z. Metallk*, 49, 1958, 280.

Seeger, A., Haasen, P. *Phil. Mag.* 3, 1958, 470.

(18-22)Wang, W.H. et al "EOS of BMGs Via Ultrasonic Method", *APL*, 79(24), 3947, 2001.

(18-22)Wang, W.H. et al, *Acta Materialia*, 52,2004, 715.



σ_2 (MPa)	Coulomb-Mohr		Drucker-Prager	
	α	k_o (MPa)	a	c (MPa)
-0.1	0.026	951	0.014	1955
-8760	0.02	800	0.01	1000



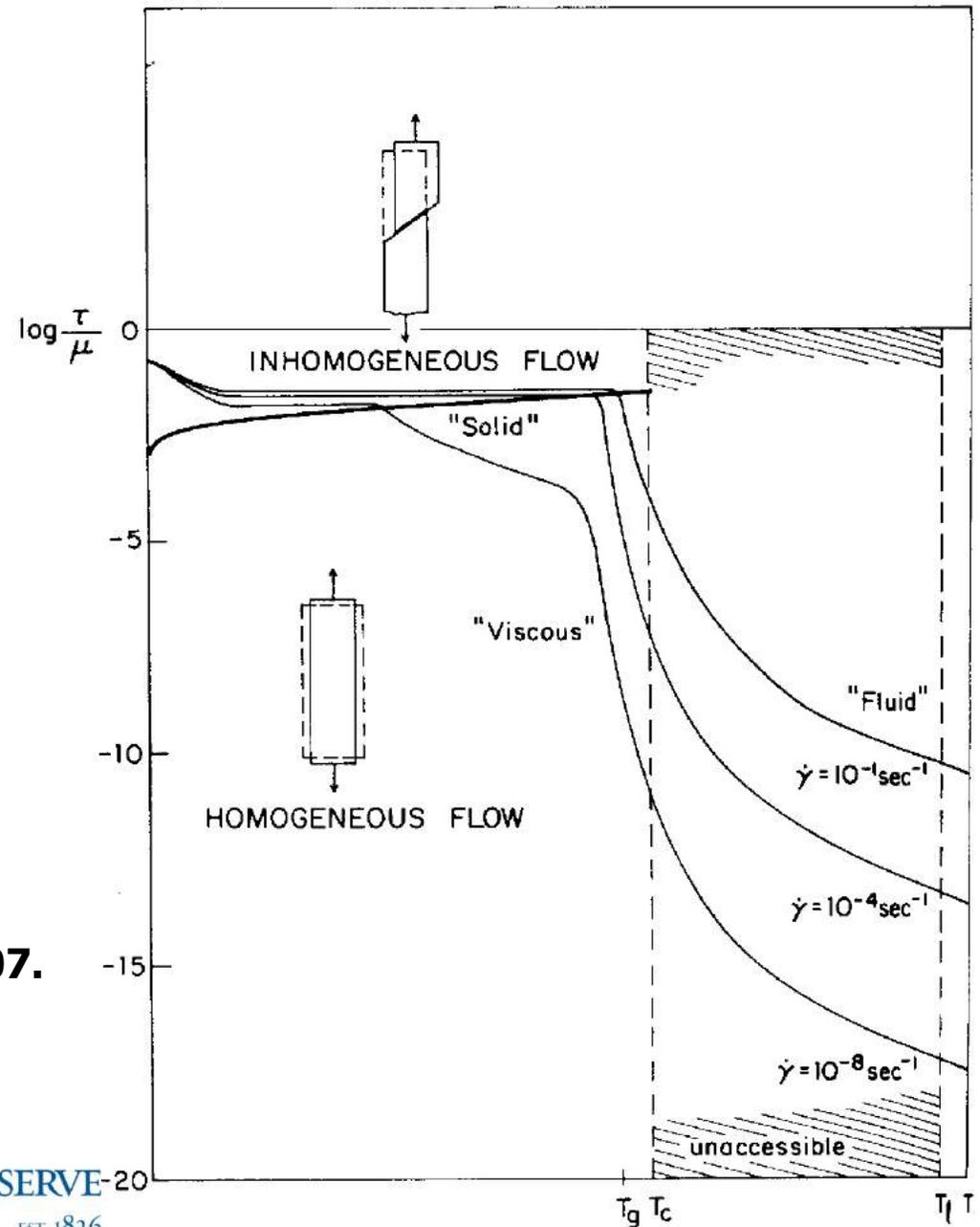
Caris, J. and Lewandowski, J.
Acta Materialia, Vol. 58, No. 3, Feb. 2010, pp. 126-136.

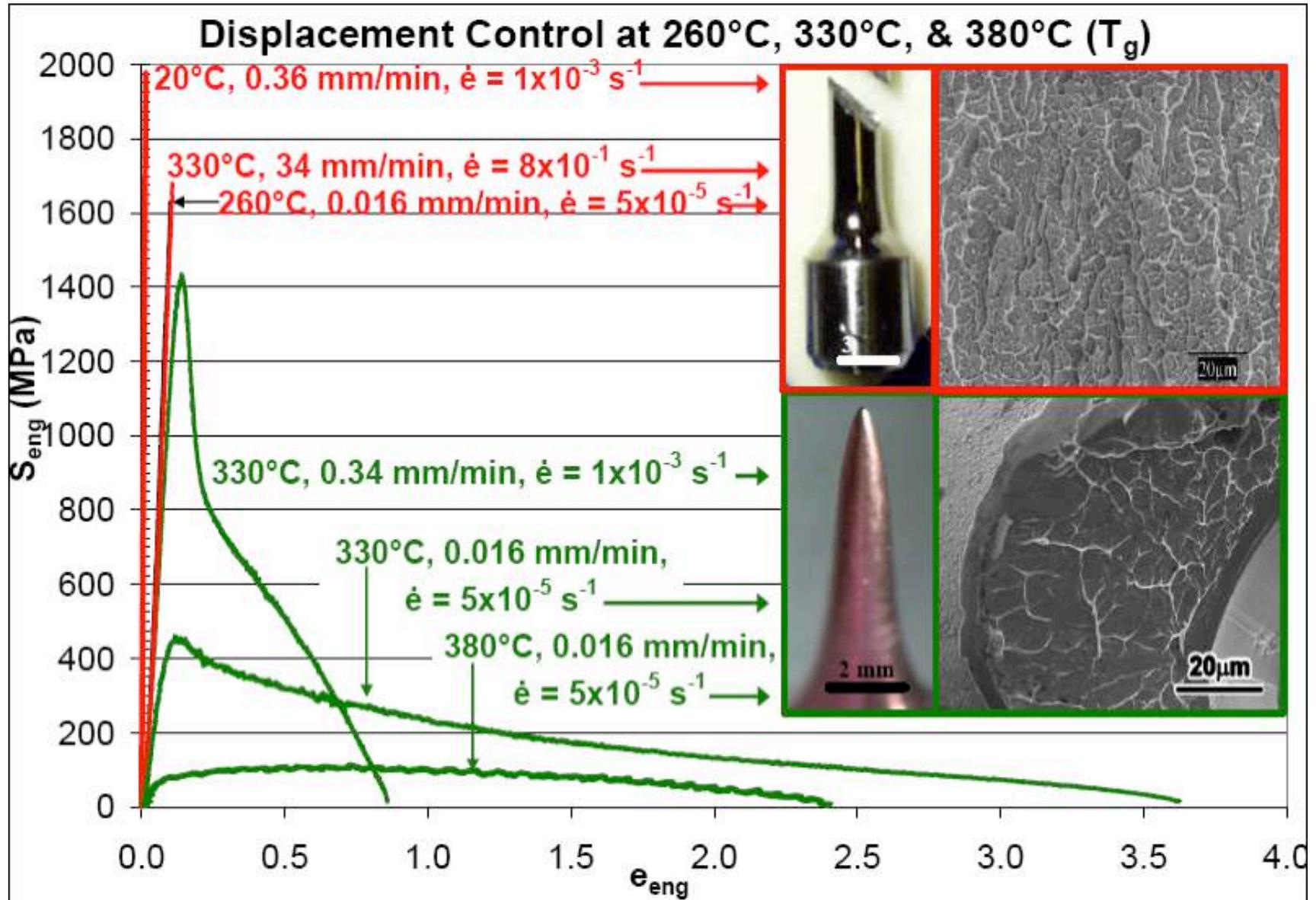


Deformation Mechanism Map

- Inhomogeneous
 - Shear Localization w/o macroscopic deformation
 - RT, near- T_g at high $\dot{\epsilon}$'s
- Homogeneous
 - Uniform Deformation
 - Superplastic
 - Near- T_g at low $\dot{\epsilon}$'s
- Effects of Pressure?
 - Implications

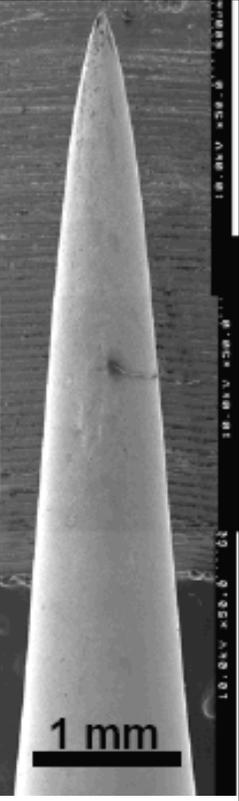
* Spaepen F. *Acta Materialia* 1979;25:407.





Tensile Results (0.1 MPa)

- **Macroscopic Appearance: Displacement Control**

20°C	260°C	330°C		380°C	
$1 \times 10^{-3} \text{ s}^{-1}$	$5 \times 10^{-5} \text{ s}^{-1}$	$5 \times 10^{-5} \text{ s}^{-1}$	$1 \times 10^{-3} \text{ s}^{-1}$	$2 \times 10^{-1} \text{ s}^{-1}$	$5 \times 10^{-5} \text{ s}^{-1}$
					



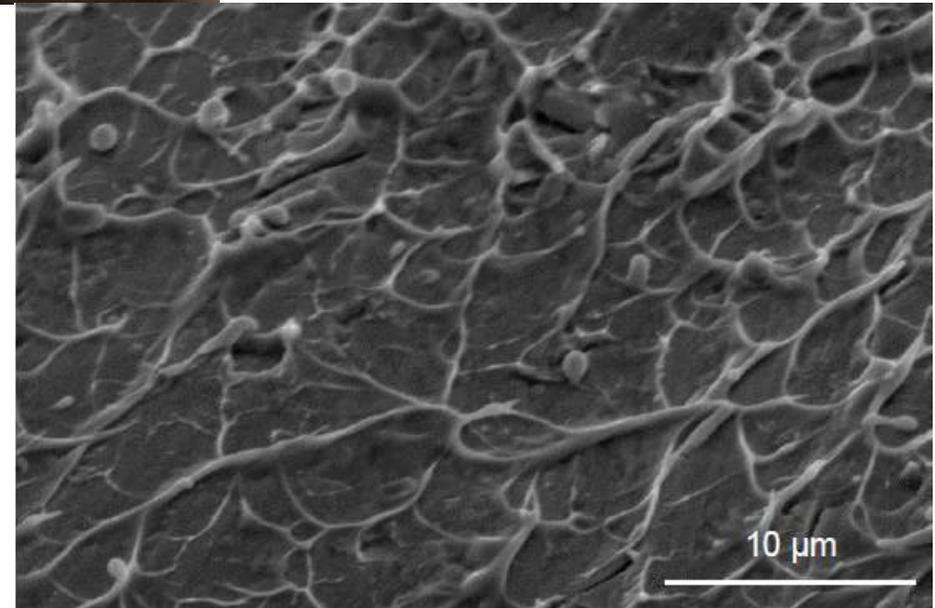
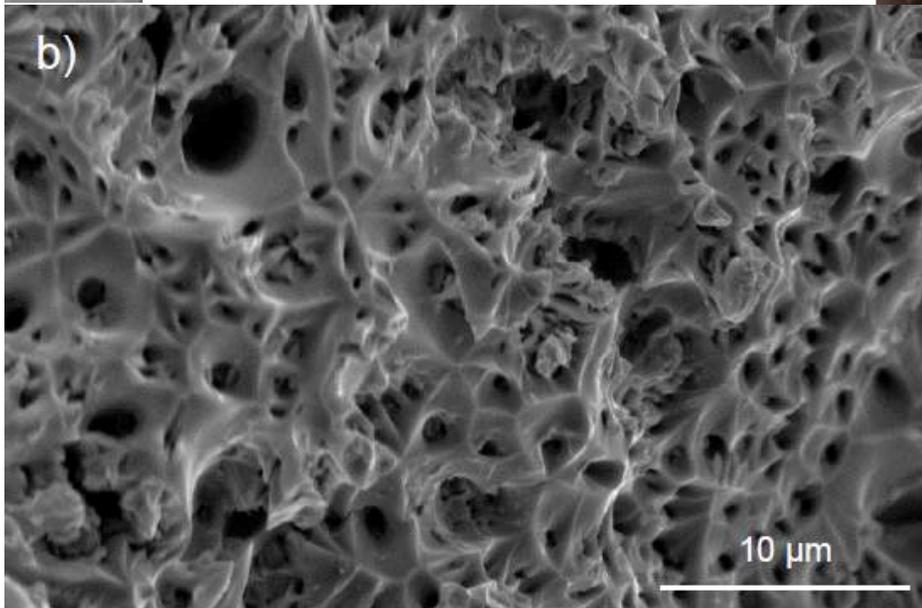
Vormelker, et al, Matls Trans A, 39A(8), 1922-1934 (2008).



$T \approx T_g$
Tension @ 0.1 MPa
Stress Overshoot Regime
Lower Strength/Viscosity
High Plasticity
Cavitation
Zr-, La-BMG



$T \approx T_g$
Tension @ Hi Pressure
Stress Overshoot Regime
High Strength/Viscosity
Reduced Plasticity
Catastrophic Shear
Zr-, La-BMG



603	0.93	0.1	497	0.00005	99	Superplastic, DNF
603 [*]	0.93	0.1	1247	0.00005	30	Shear
603 ^{**}	0.93	0.1	1604	0.00005	3	Shear
603	0.93	200	N/A	0.4	19	Shear
603	0.93	264	1246	0.5	25	Shear
603	0.93	199	1013 ⁺	0.6	>10 ⁺	DNF
603	0.93	446	1699	0.9	2	Shear
607	0.93	280	N/A	0.56	5	Shear

**T(K) T/T_g P(MPa) σ_f P/UTS @
0.1 MPa RA% Fracture
Mode**

Large Effects of Pressure as T \approx T_g (Zr-BMG)

- Effects Greatest at Stress Overshoot Conditions (603K) ***/** High Strain Rate**
- Pressure-Induced Increases in Strength/Viscosity
- Pressure-Induced Decreases in Ductility (Superplastic-Shear)



Vatamanu et al, Mechanics of Materials, **67**, pp. 86-93 (2013).



T (K)	T/T _g	P (MPa)	σ_f (MPa)	(P/UTS @ 0.1 MPa)	RA (%)	Fracture mode
298	0.69	0.1	650	0.0016	6	Shear
298	0.69	170	604	0.26	3	Shear
298	0.69	239	624	0.36	0	Shear
373	0.88	0.1	347	0.0003	89	Neck, cavitation
383	0.91	165	416	0.55	0	Shear
398	0.94	0.1	103 ⁺	0.001	61 ⁺	DNF
398	0.94	106	333	1.4	23	Neck+Shear
398	0.94	235	231	3.1	30	Neck+Shear

Large Effects of Pressure as $T \approx T_g$ (La-BMG)

- Effects Greatest at Stress Overshoot Conditions (373-383K)
- Pressure-Induced Increases in Strength/Viscosity
- Pressure-Induced Decreases in Ductility

(Superplastic Transition to Catastrophic Shear)

Vatamanu et al, Mechanics of Materials, 67, pp. 86-93 (2013).

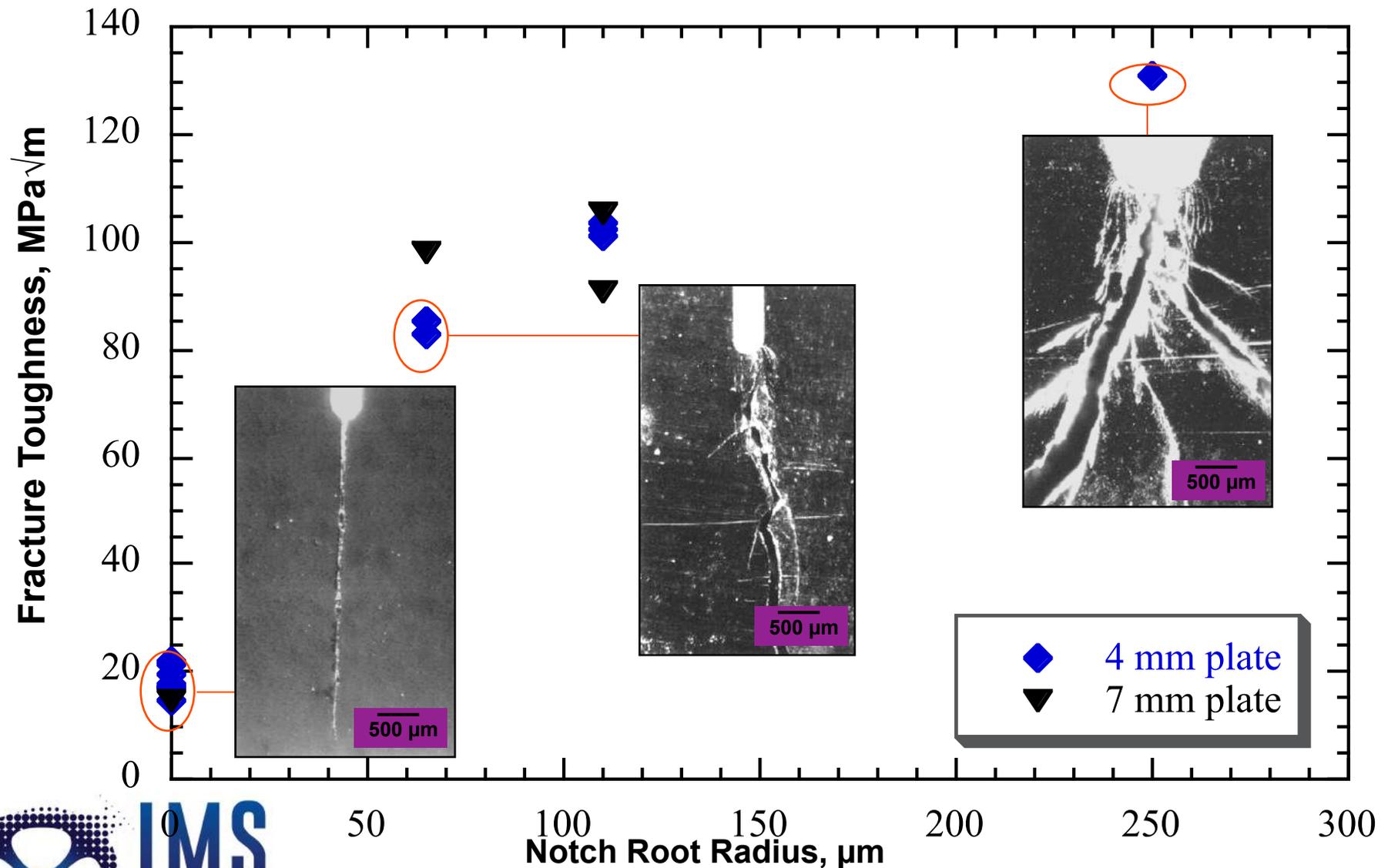


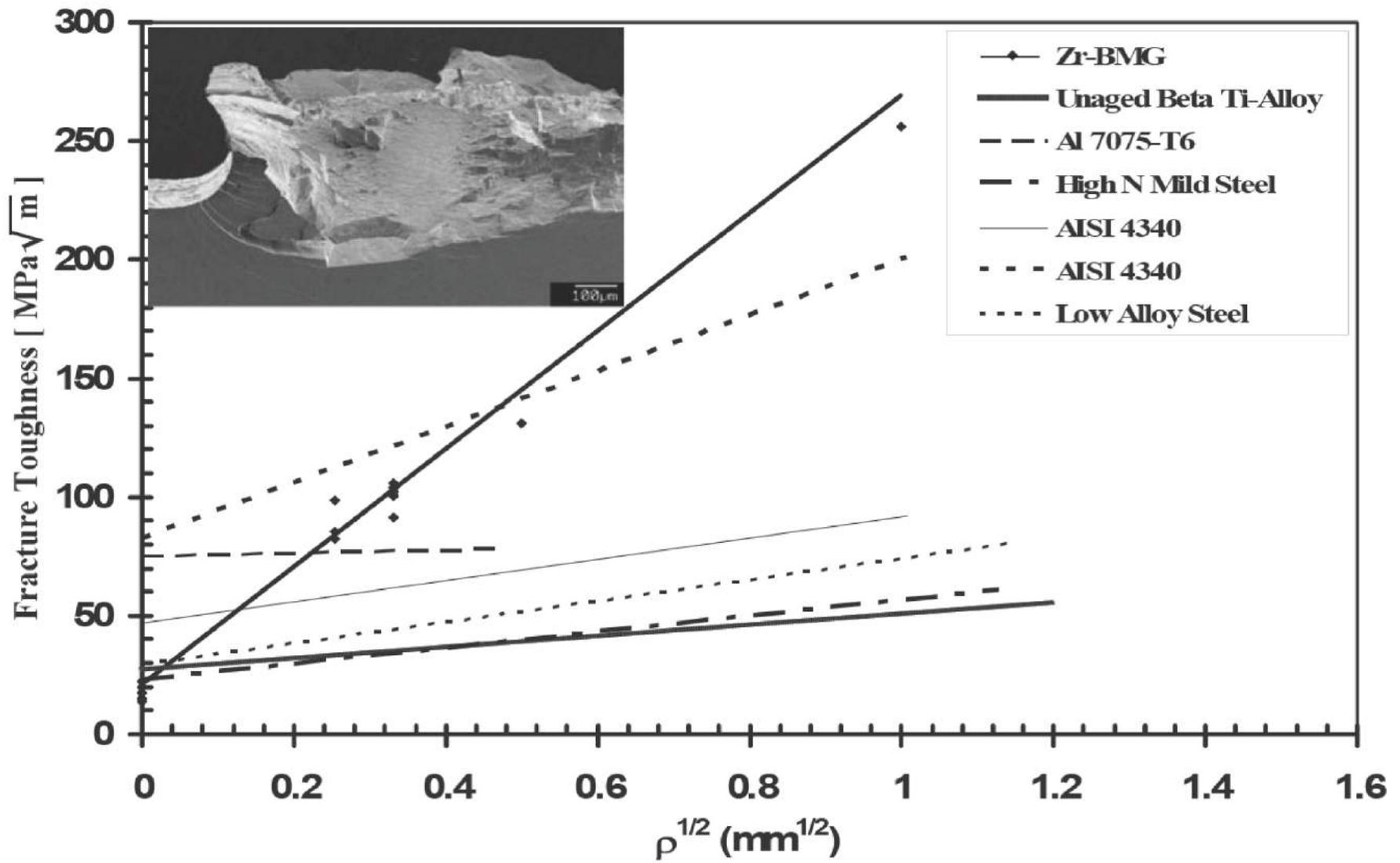
Outline

- **Stress State Effects on Flow/Fracture of BMGs at RT ($T \ll T_g$)**
 - Minimal Effect of Superimposed Pressure on Strength/Plasticity
- **Stress State and Temperature Effects on BMGs ($T \approx T_g$)**
 - BIG Effects of Superimposed Pressure on Strength/Plasticity (Strength/Viscosity $\uparrow\uparrow$, Plasticity $\downarrow\downarrow$)
- **Quasi-Static Fracture Behavior**
 - Fracture Behavior/Damage Tolerance
 - Notch/Fracture Toughness
 - Effects of Chemistry Changes/Annealing-Induced Embrittlement
 - Correlation with Elastic Constants
 - Alloy Design - Fe-based BMG, Ti-based BMG
 - Toughening Approaches
- **Creation of Micro/Nano Metallic Glass Wires**
 - Review of Recent Techniques
 - Initial Testing of Micro/Nano Wires
 - Effects of Sample Size and Preparation on Plasticity
- **Advanced/Additive Manufacturing**



Effects of Notch Root Radius on Fracture Profile and Toughness of Zr-Ti-Ni-Cu-Be Bulk Metallic Glass

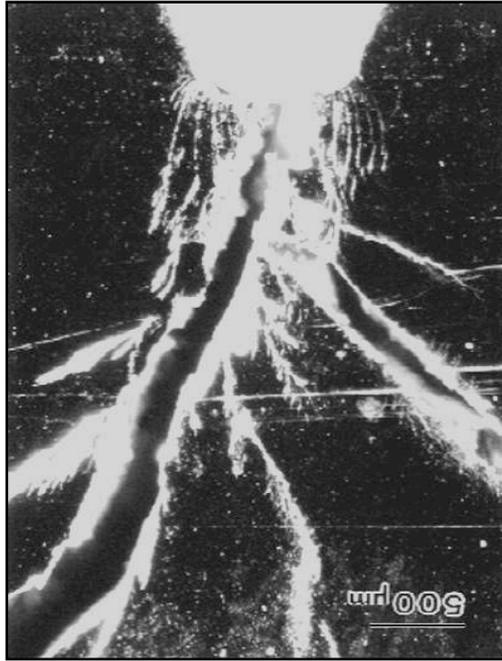




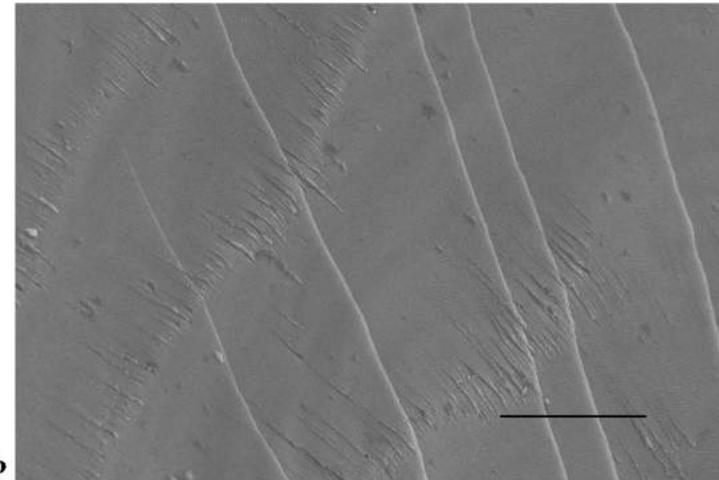
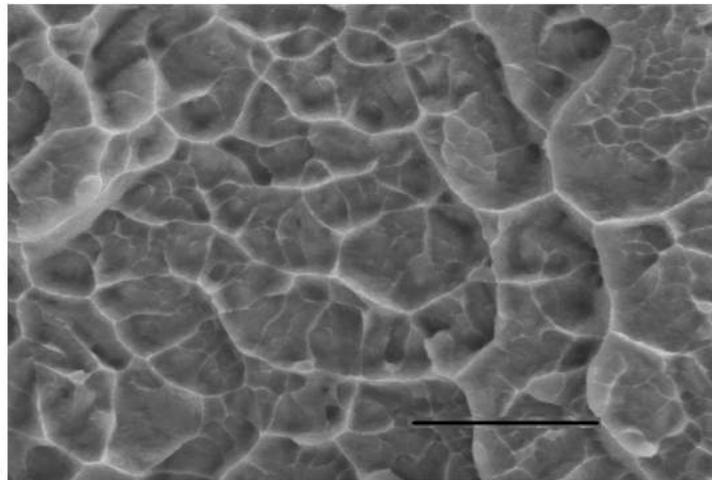
JJ Lewandowski, M Shazly, A Shamimi Nouri, Scripta Mater., 2006; 54(3), 337.



TOUGH

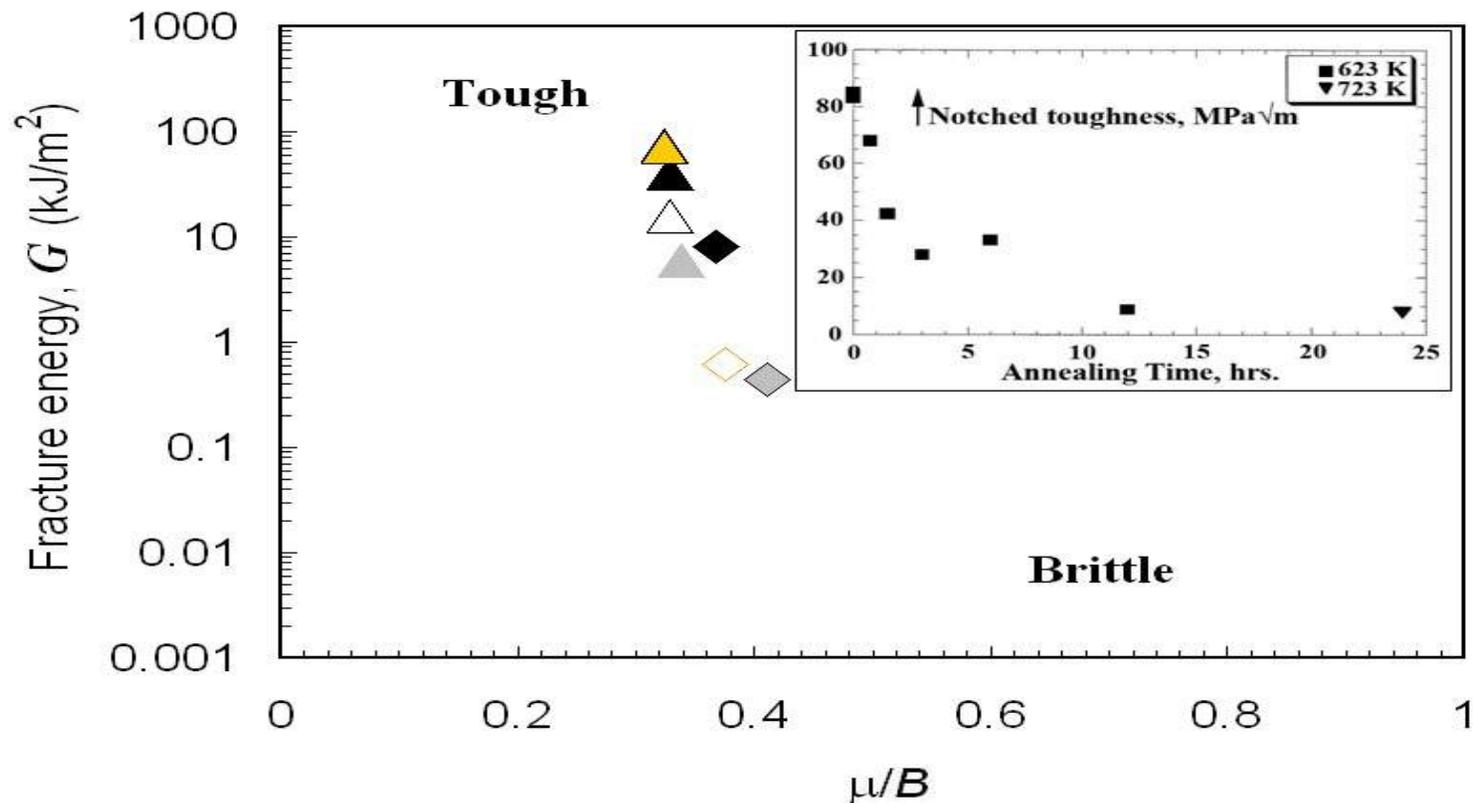


BRITTLE



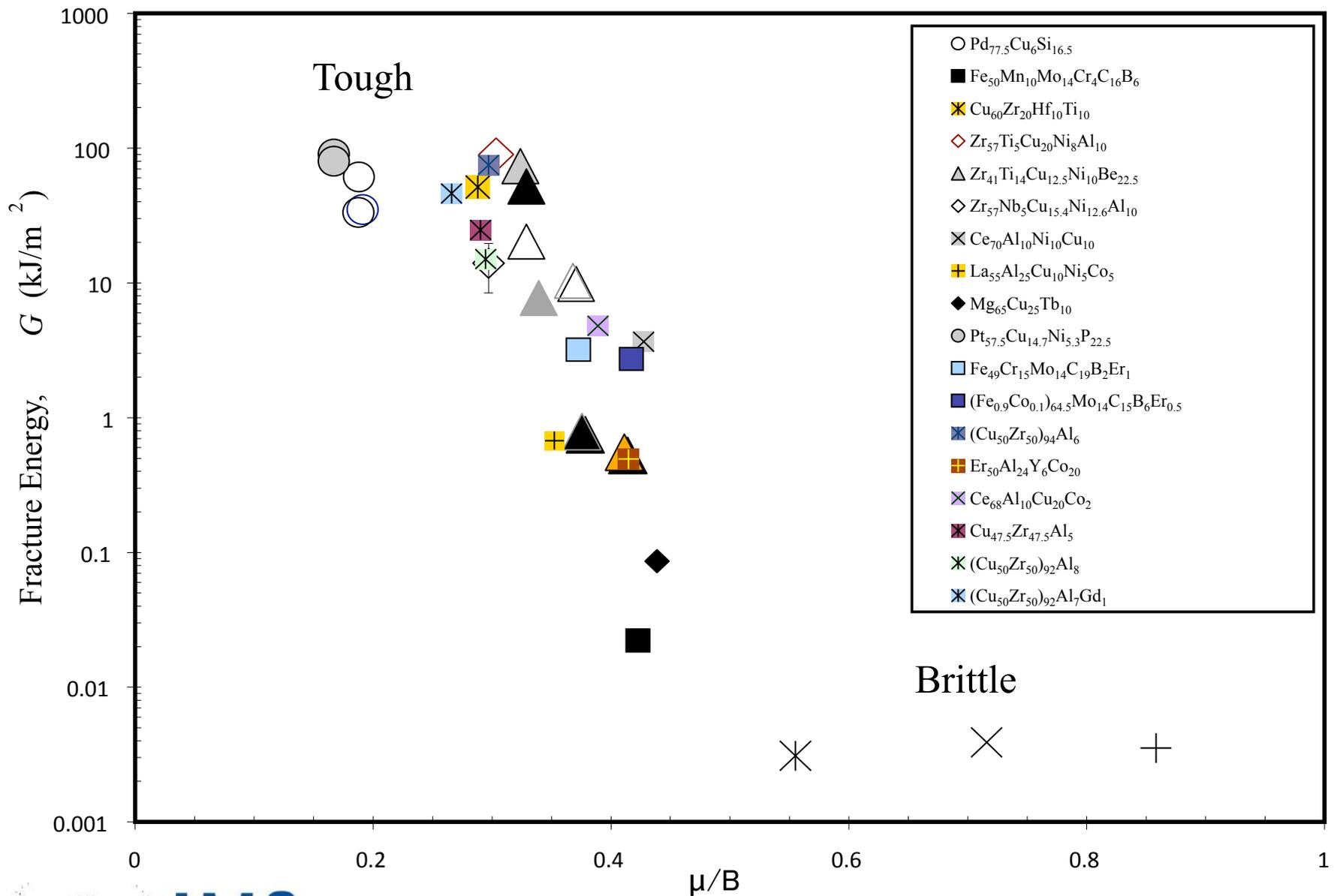
PLASTICITY OR BRITTLINESS OF METALLIC GLASSES

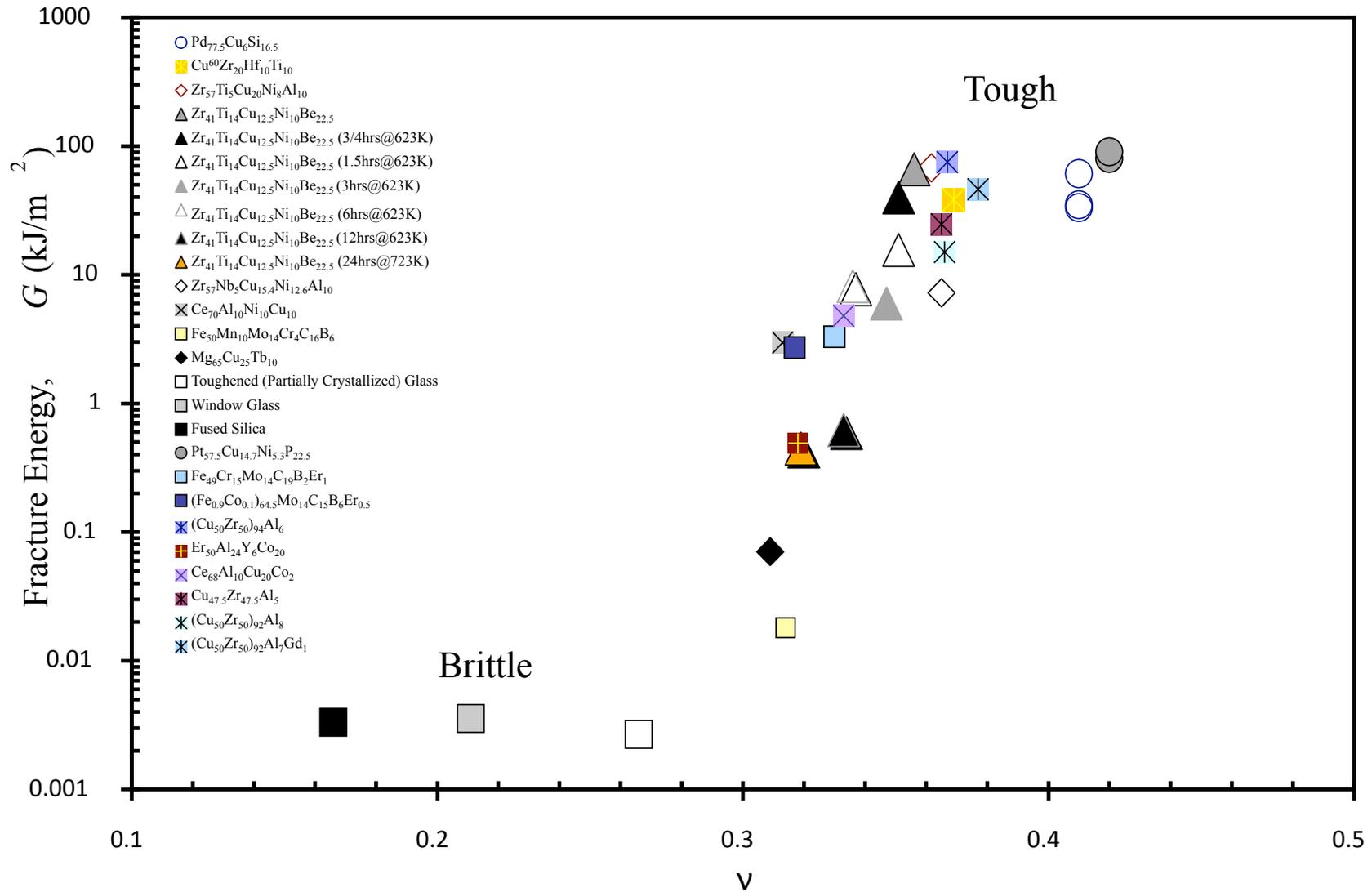
- **Amorphous Metals: (Competition Flow/Fracture)**
 - **Isotropic elastic constants**
 - Resistance to shear controlled by shear modulus, μ
 - Resistance to dilatation controlled by bulk modulus, B
 - Crack tip stresses produce dilatation
 - Low μ/B favors plasticity?
 - High μ/B favors brittleness?
 - How to measure plasticity/brittleness?
 - Fracture Energy = $G = 2\gamma$
 - $G = K^2(1-\nu^2)/E$
 - **Elastic constants more easily measured in bulk metallic glasses**
 - W.H. Wang - Chinese Academy Sciences
 - Joe Poon - Univ. Virginia
 - A. Kelly/A.H. Cottrell - University Cambridge
 - A.L. Greer - University of Cambridge
 - D. Schuele - CWRU



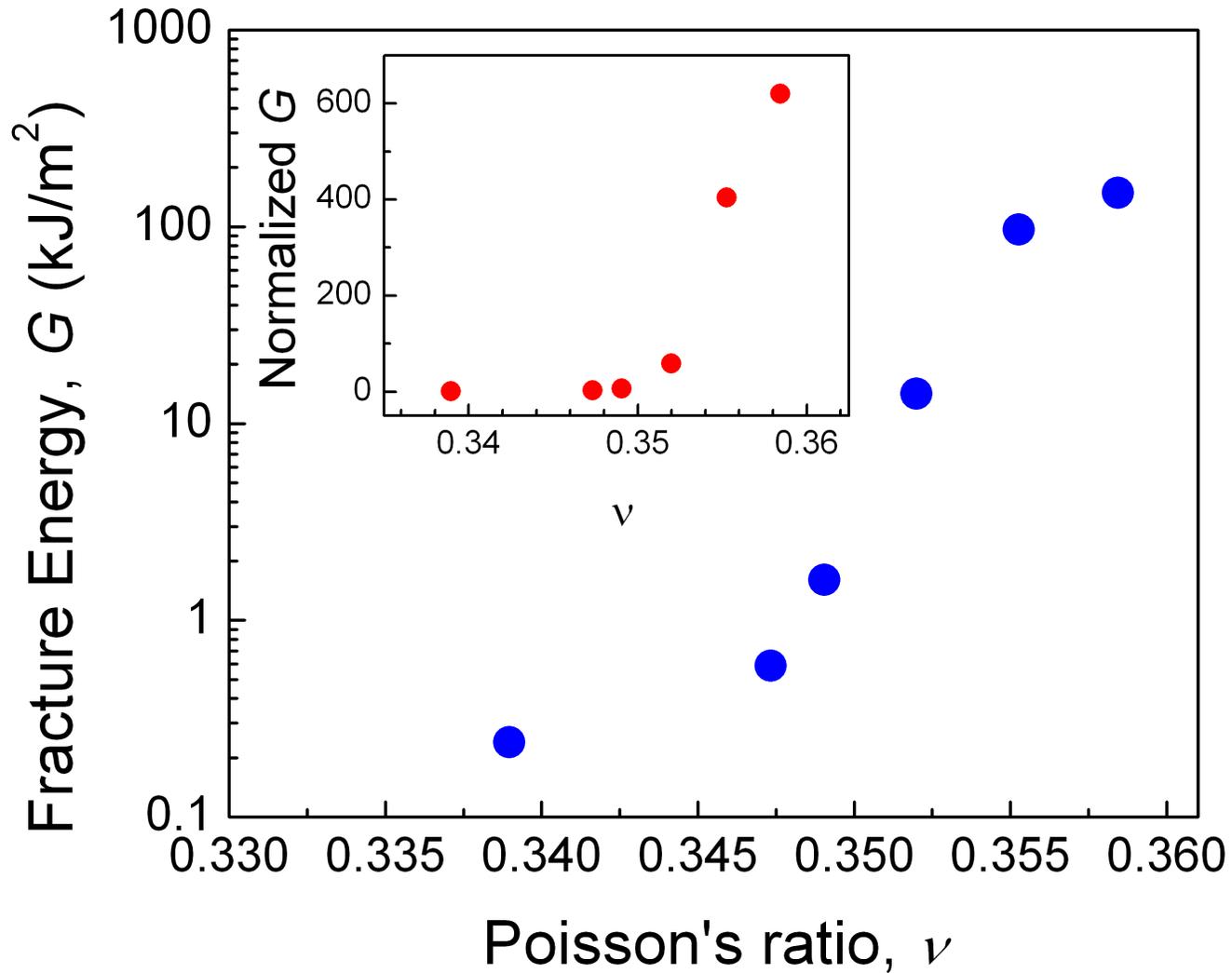
- ▲ As - Cast ▲ 3/4 hrs @ 623 K △ 1.5 hrs @ 623 K
 ▲ 3 hrs @ 623 K ◆ 6 hrs @ 623 K ◇ 12 hrs @ 623 K
 ◇ 24 hrs @ 723 K

Inset shows decrease in toughness with annealing time for Vitreloy 1. Figure shows a good correlation of embrittlement with changing μ/B .



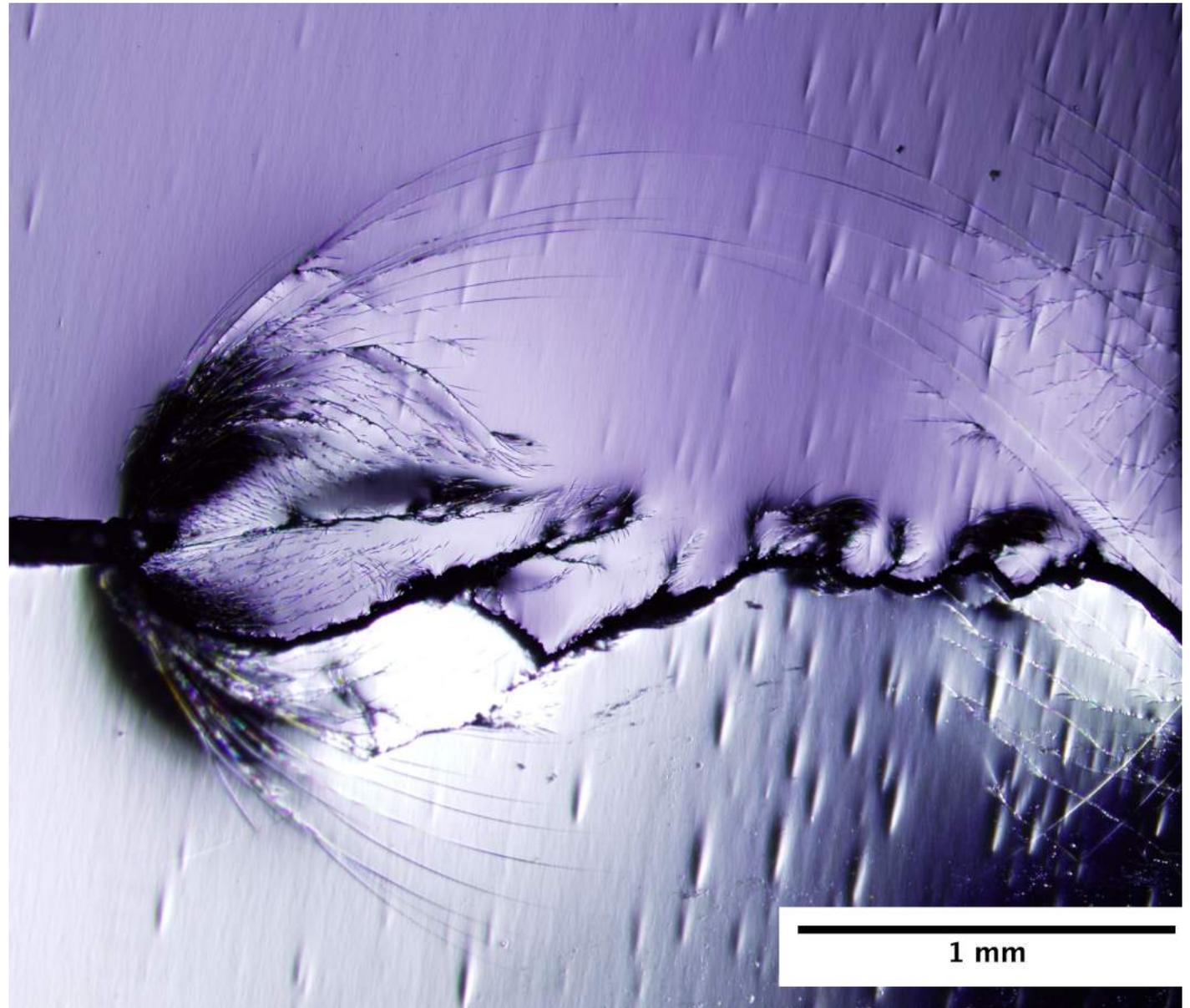


Ti-Based BMG (5 mm thick)

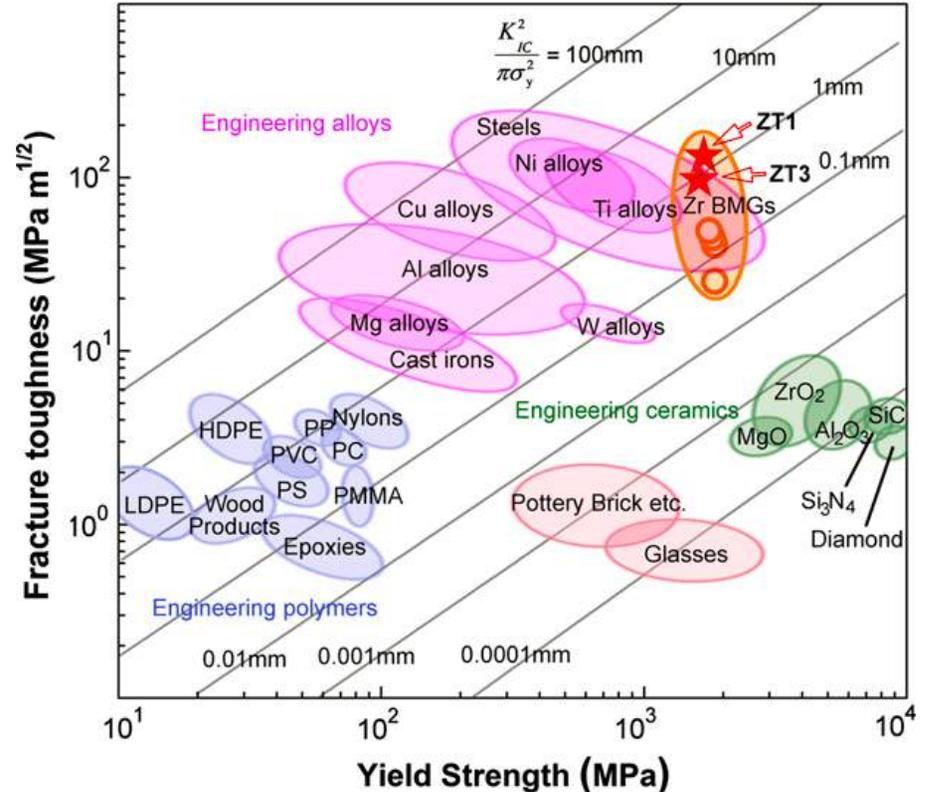
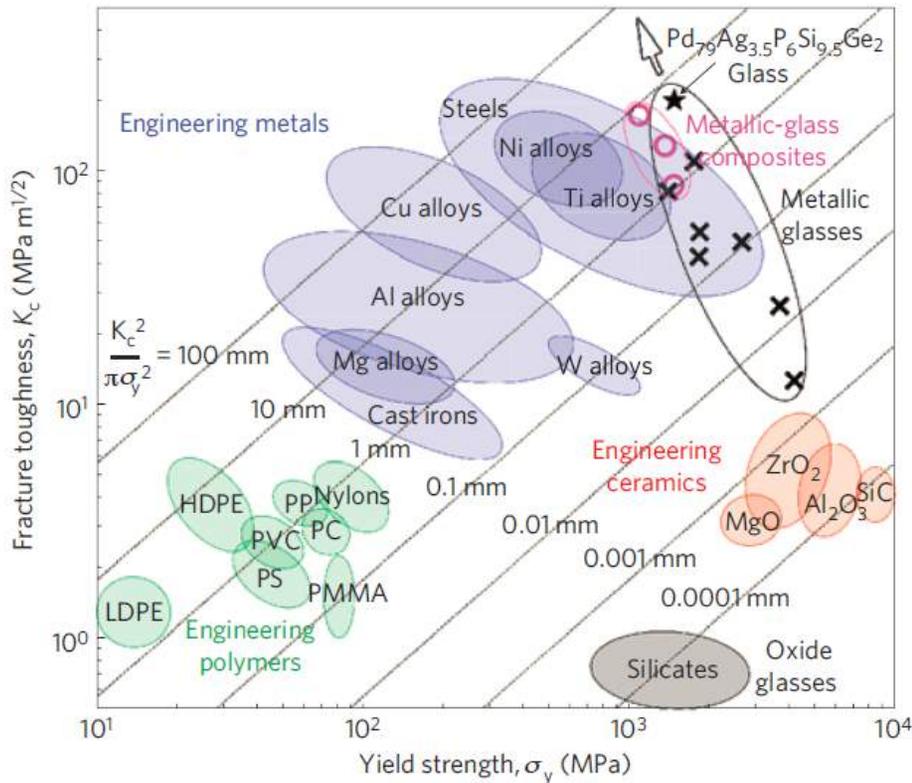


$K_{Ic} > 110 \text{ MPa}\cdot\text{m}^{1/2}$

Thickest and toughest
BMG to date



Damage-tolerant BMGs



***Nature Mater.* 10, 123 (2010)**

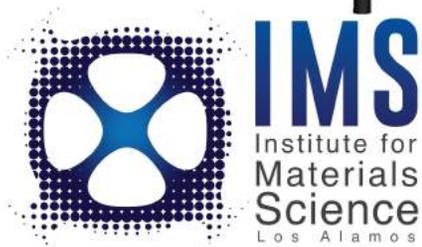
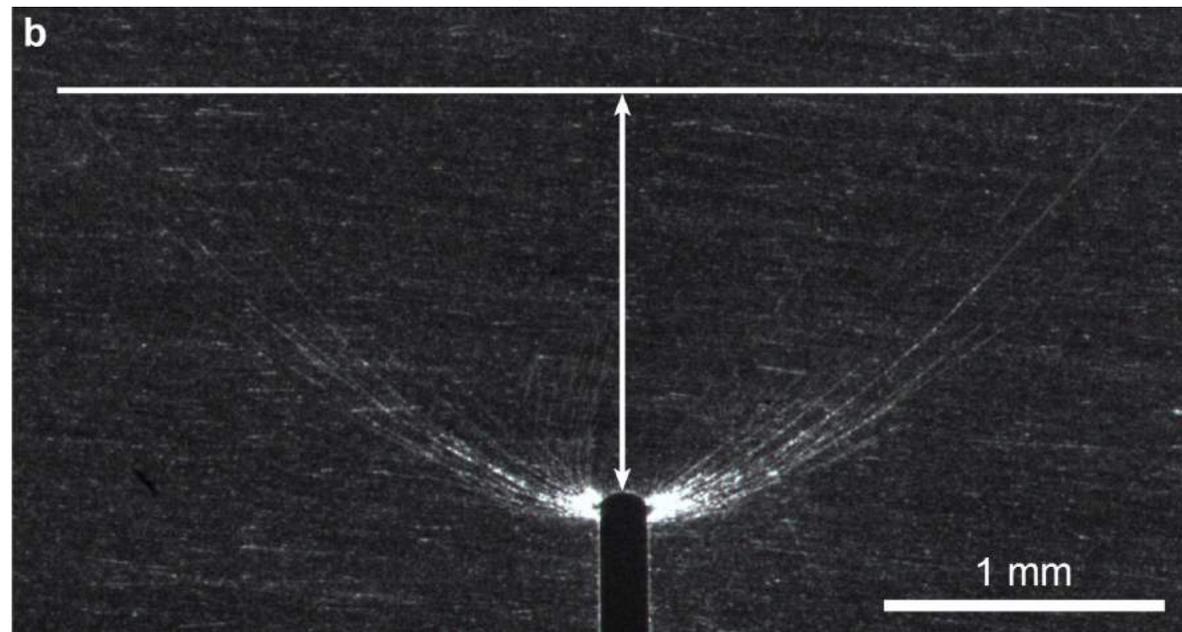
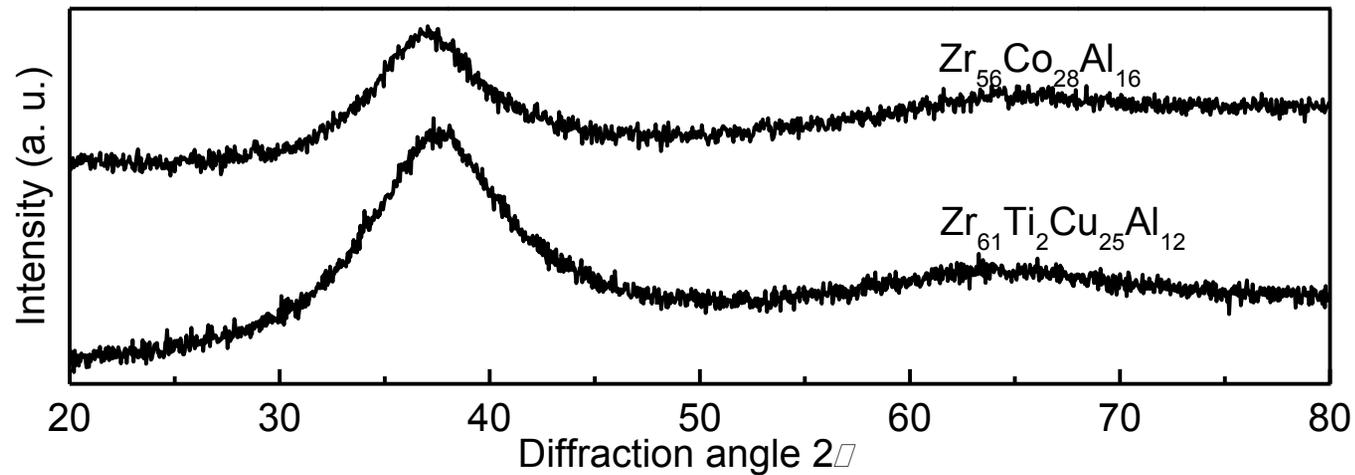


***Acta Mater.* 58, 1708 (2010)**

***Acta Mater.* 60, 4940 (2012)**

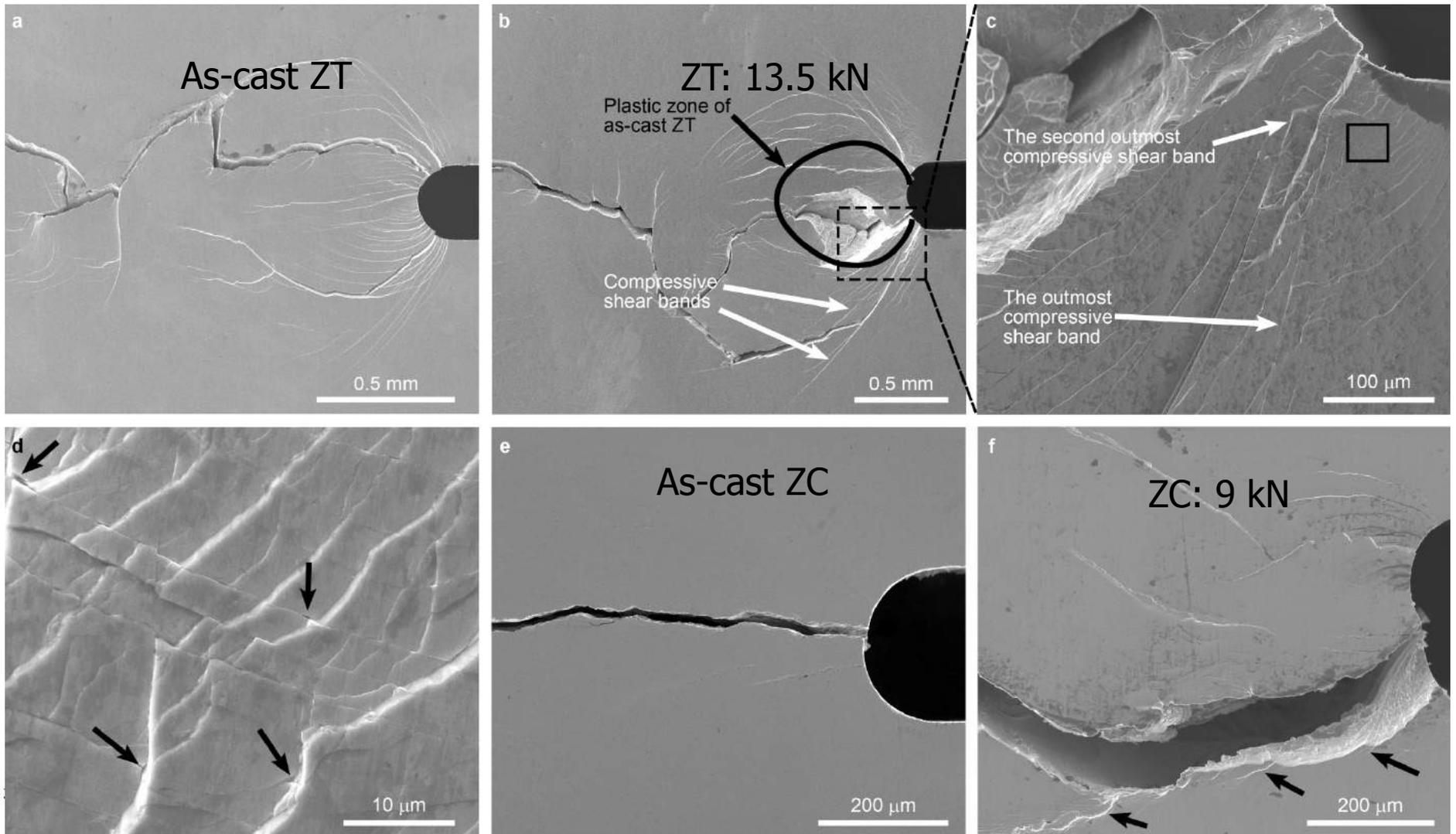


Another toughening strategy

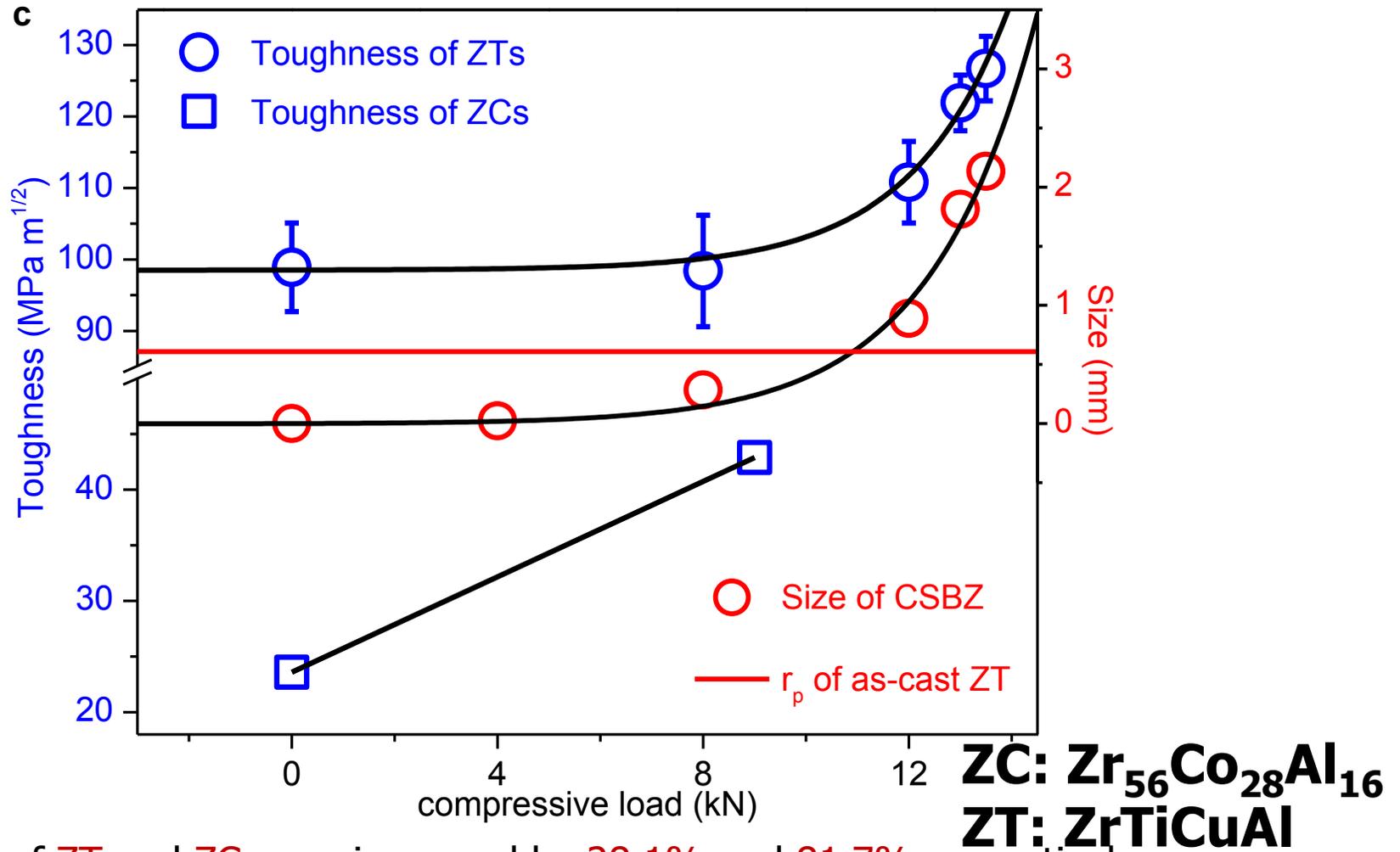


Jun Yi, Wei Hua Wang and John J. Lewandowski
Advanced Eng. Matl's, 17(5), pp. 620-625.

Crack deflection enhanced in pre-compressed BMGs



Toughness Improvement of ZT & ZC



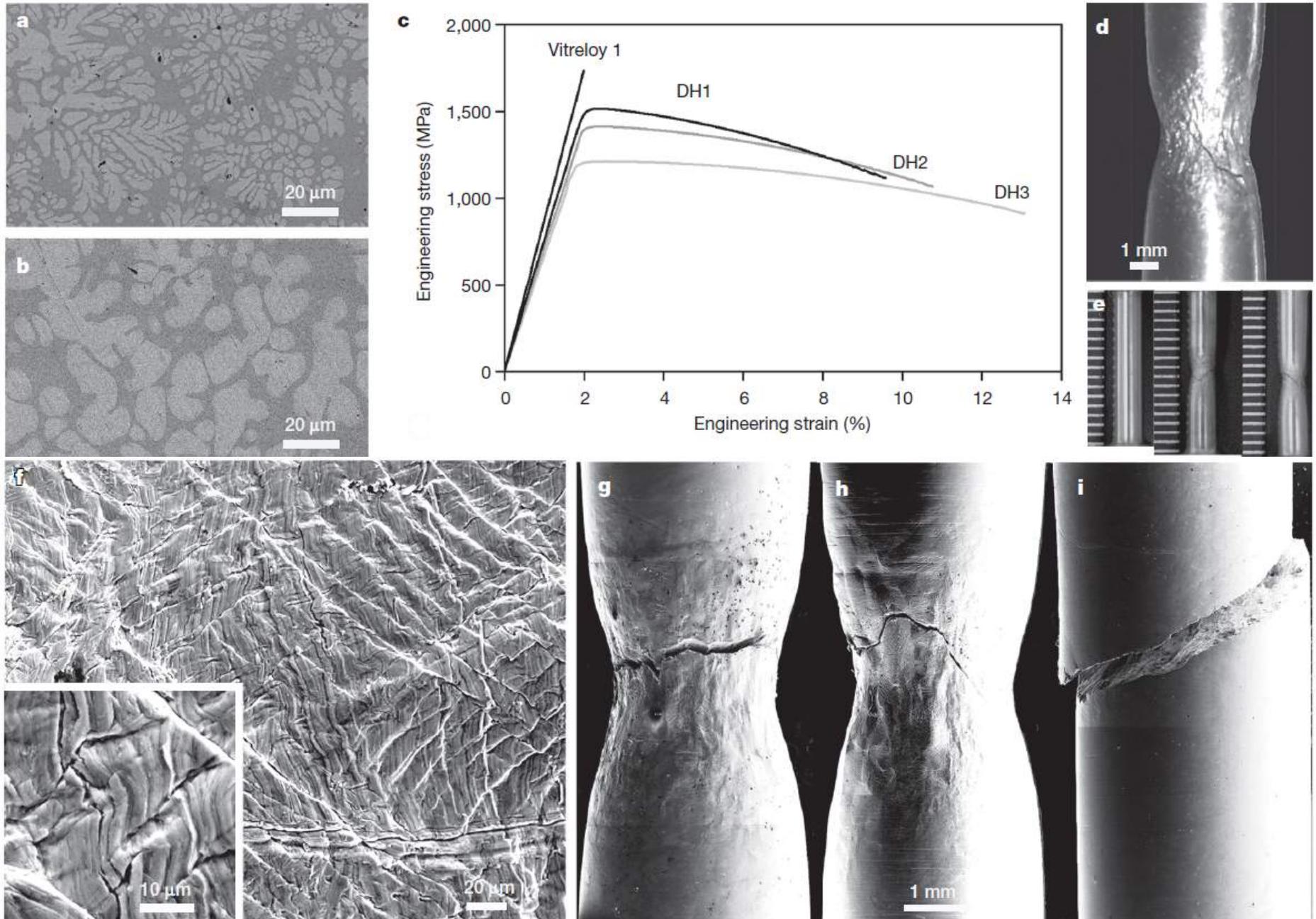
Toughness of **ZT** and **ZC** were improved by **28.1%** and **81.7%** respectively.

CSBZ: compressive shear band zone



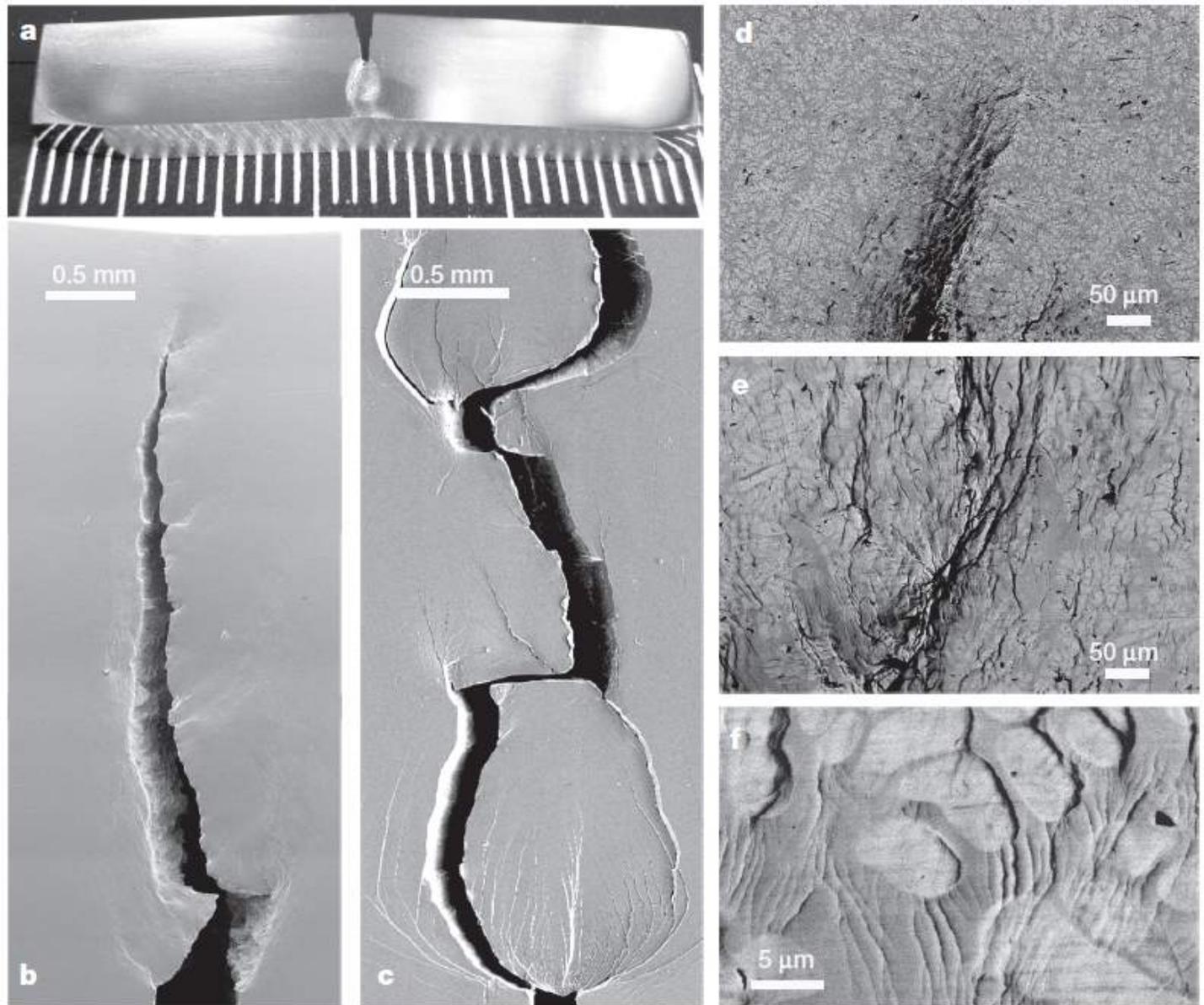
Jun Yi, Wei Hua Wang and John J. Lewandowski
 Advanced Eng. Matl's, **17(5)**, pp. 620-625.

Hoffman et al, Nature (2010) Composite Approaches



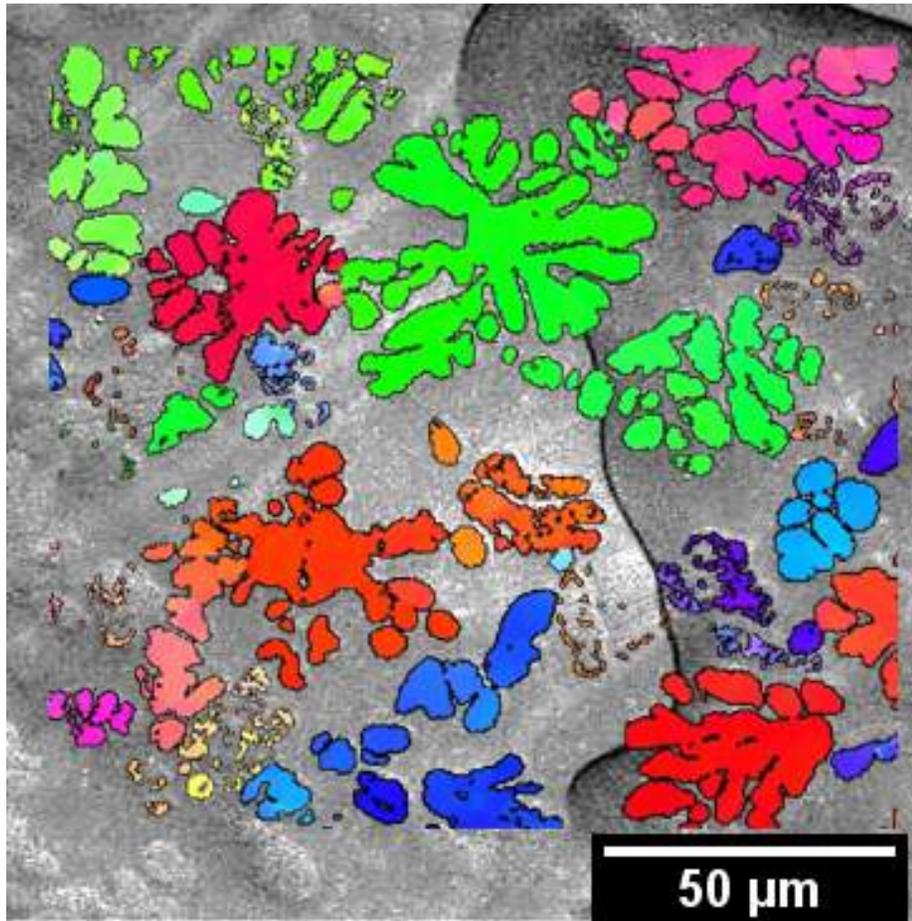
Hoffman et al,
Nature
(2010)

$K_{Ic} > 150 \text{ MPa}\cdot\text{m}^{1/2}$

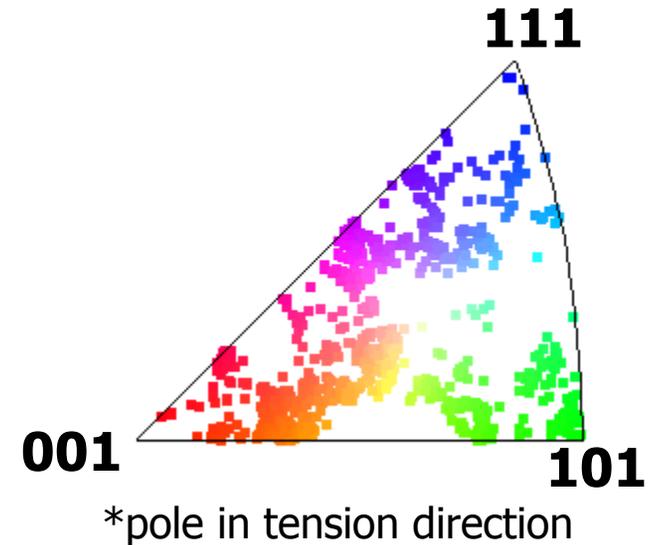


Jennifer Carter – CWRU (Effects of Orientation)

IPF Map Overlay



- All dendrites represented
- IPF indicates random texture
- Indexed: 40.5%
- # Dendrites: 21



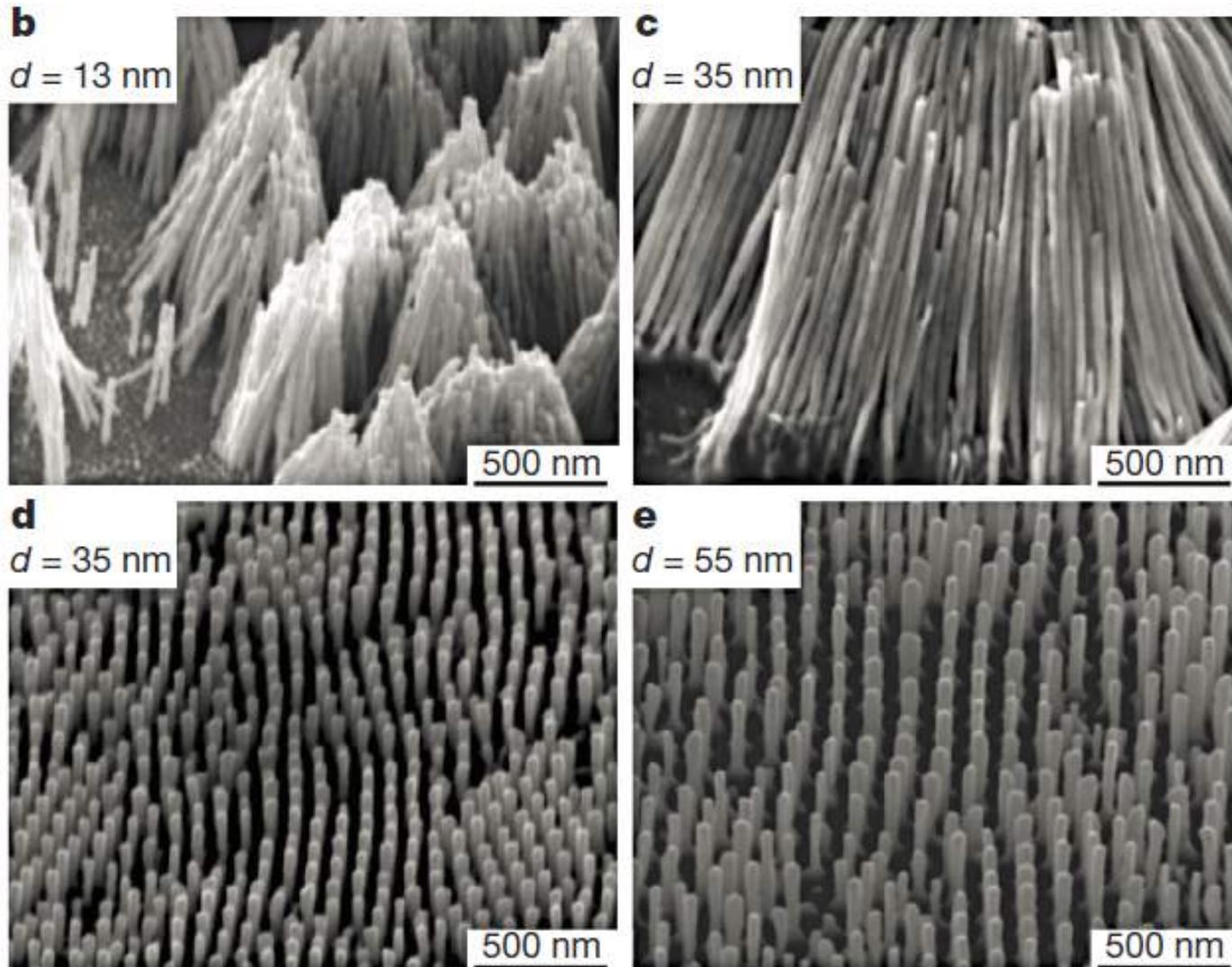
σ_a 

Outline

- **Stress State Effects on Flow/Fracture of BMGs at RT ($T \ll T_g$)**
 - **Minimal Effect of Superimposed Pressure on Strength/Plasticity**
- **Stress State and Temperature Effects on BMGs ($T \approx T_g$)**
 - **BIG Effects of Superimposed Pressure on Strength/Plasticity (Strength/Viscosity $\uparrow\uparrow$, Plasticity $\downarrow\downarrow$)**
- **Quasi-Static Fracture Behavior**
 - **Fracture Behavior/Damage Tolerance = $f(\mu/B, v)$**
 - Alloy Design - Fe-based BMG, Ti-based BMG
- **Creation of Micro/Nano Metallic Glass Wires**
 - **Review of Recent Techniques**
 - **Initial Testing of Micro/Nano Wires**
 - **Effects of Sample Size and Preparation on Plasticity**
- **Advanced/Additive Manufacturing**
 - **Metallic Glasses**

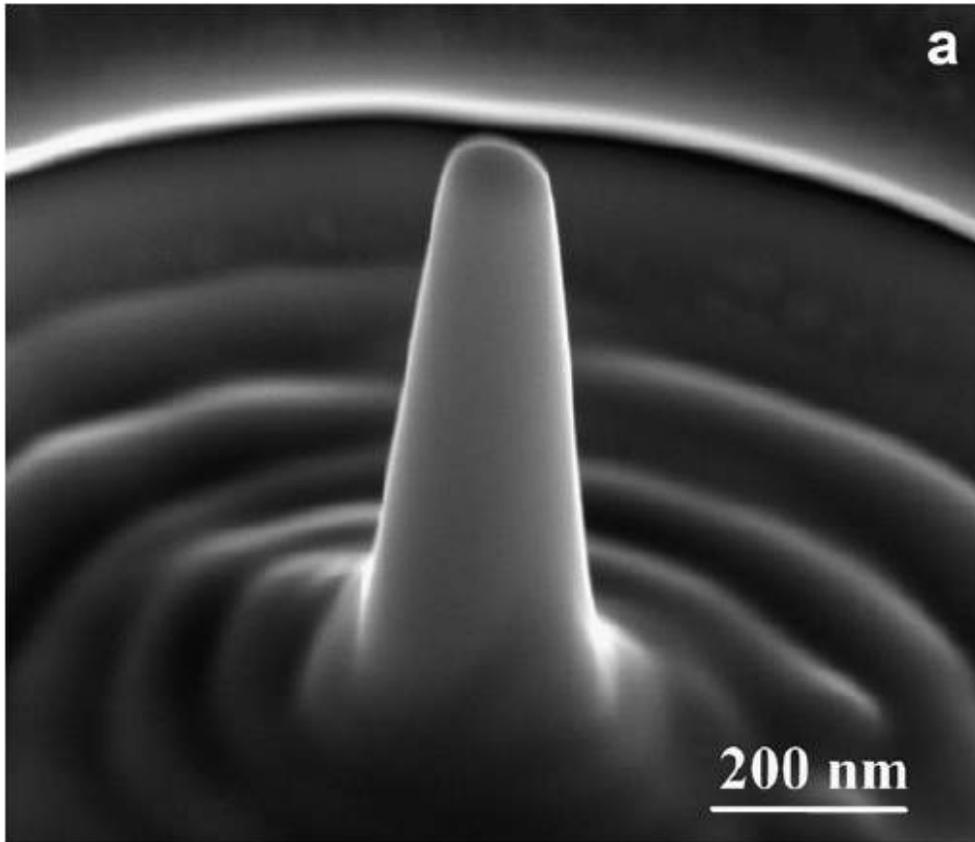


Nanomoulding

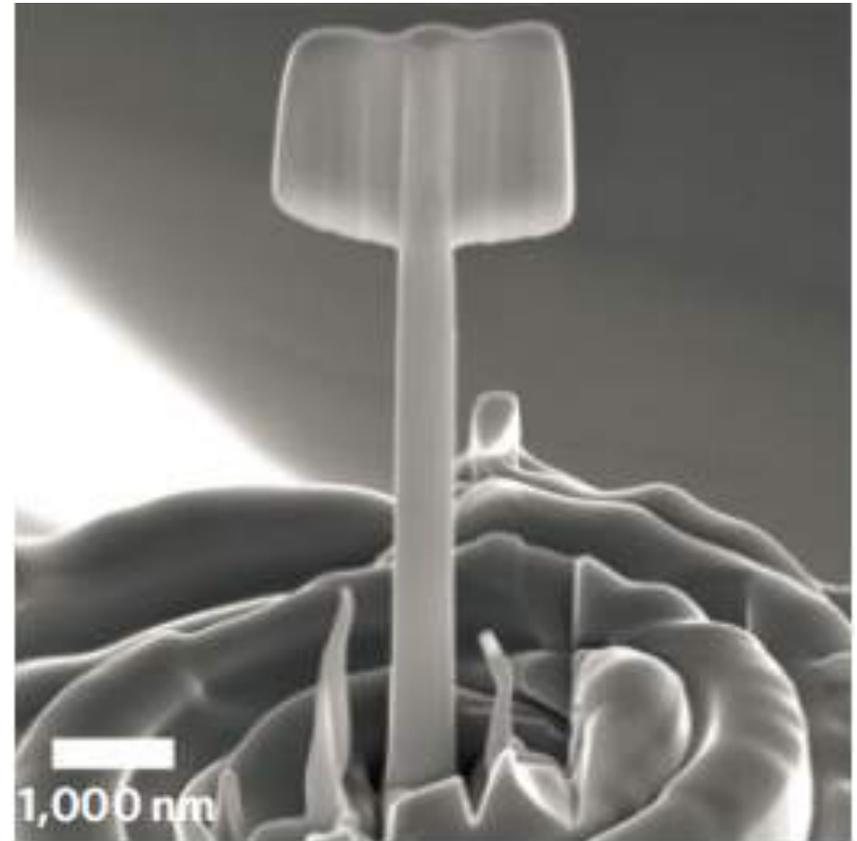


FIB Milling

Compression



Tension



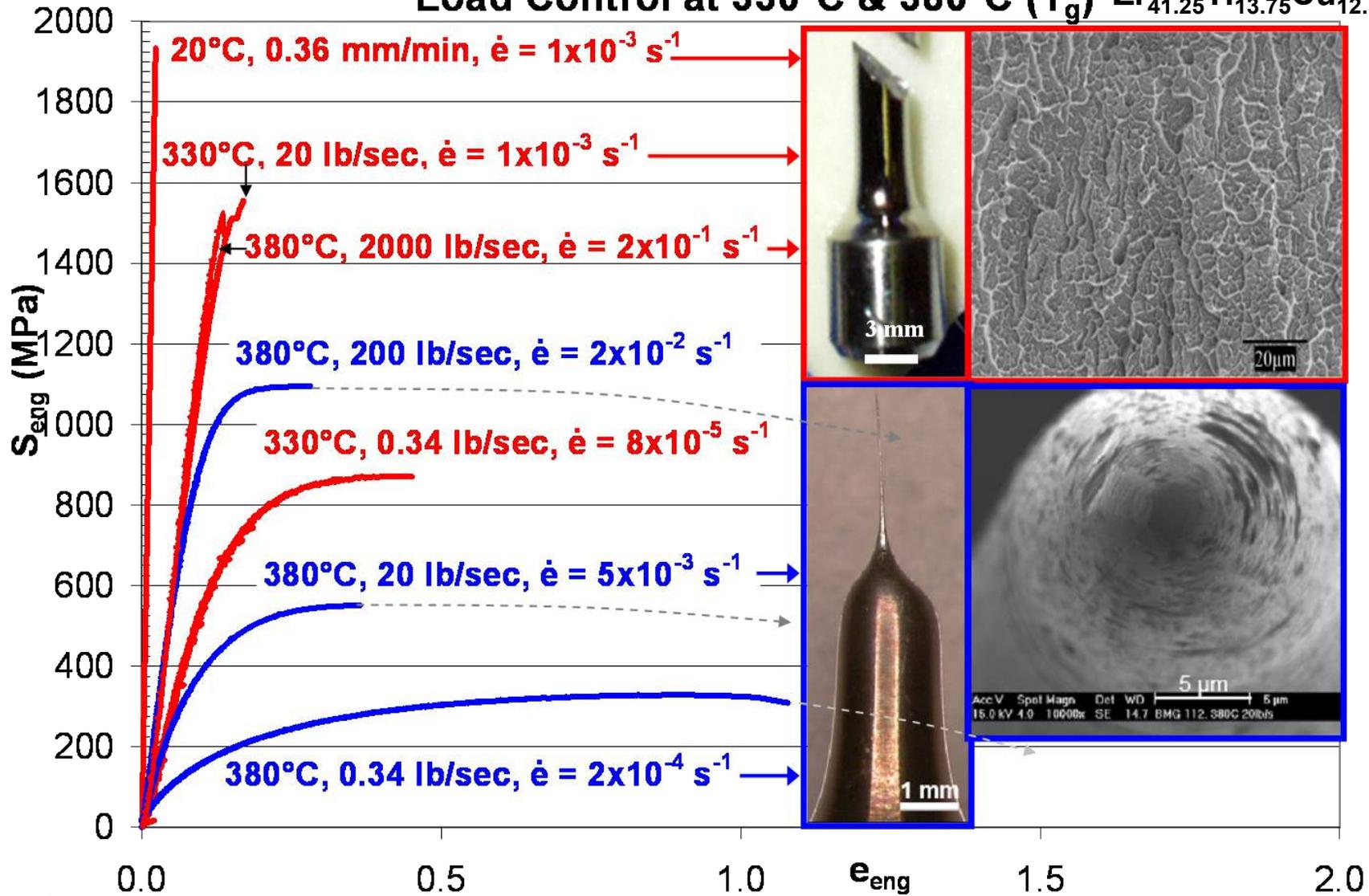
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Acta Mater. 2008 , 56, 5091

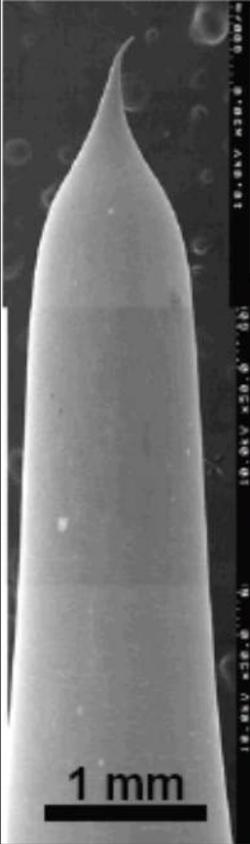
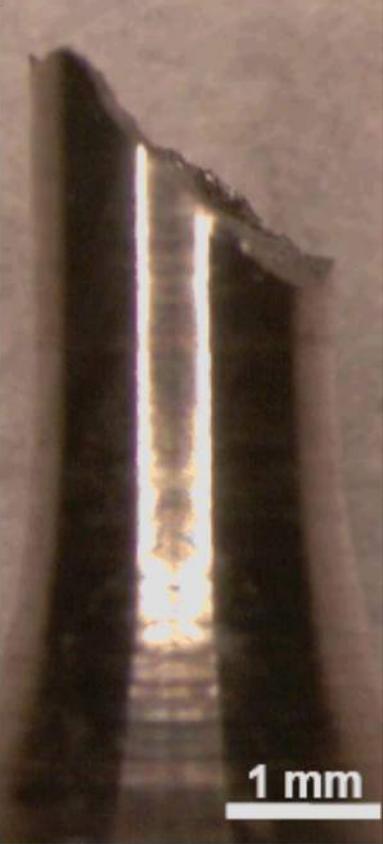
Nature Mater. 2010, 9, 215

 **CASE WESTERN RESERVE**
UNIVERSITY EST. 1826

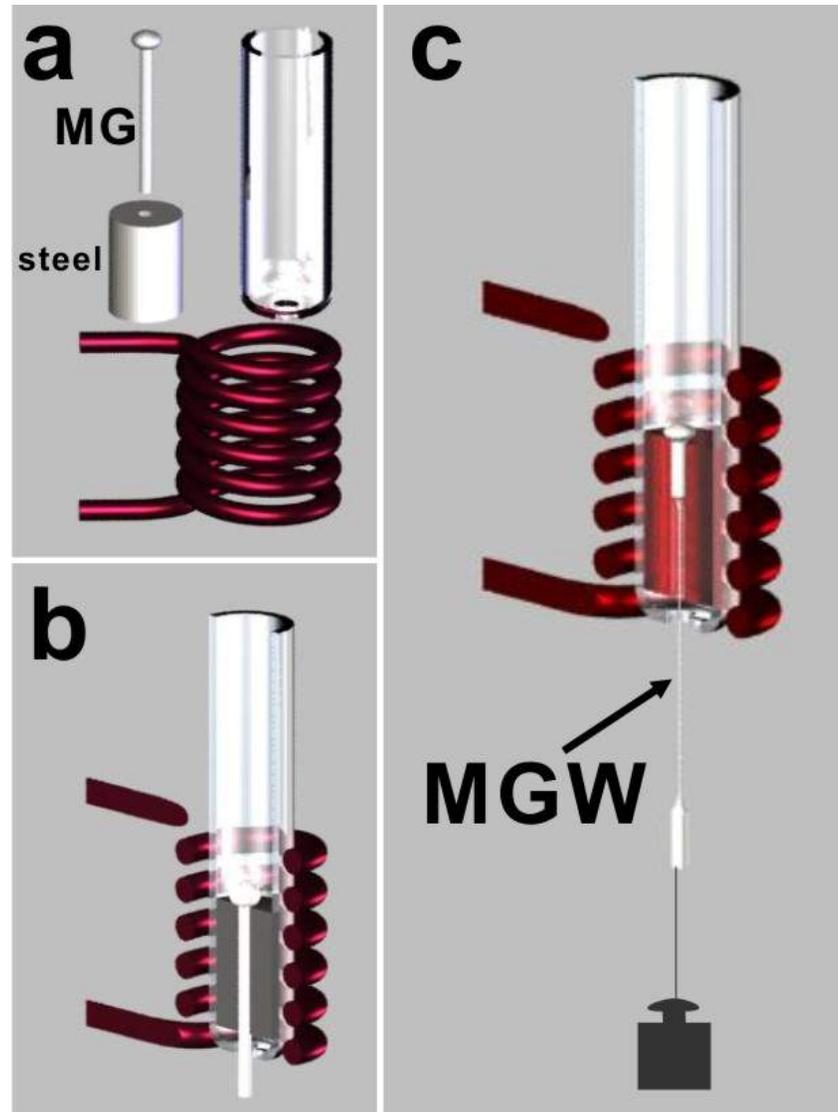
Load Control at 330°C & 380°C (T_g) $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$



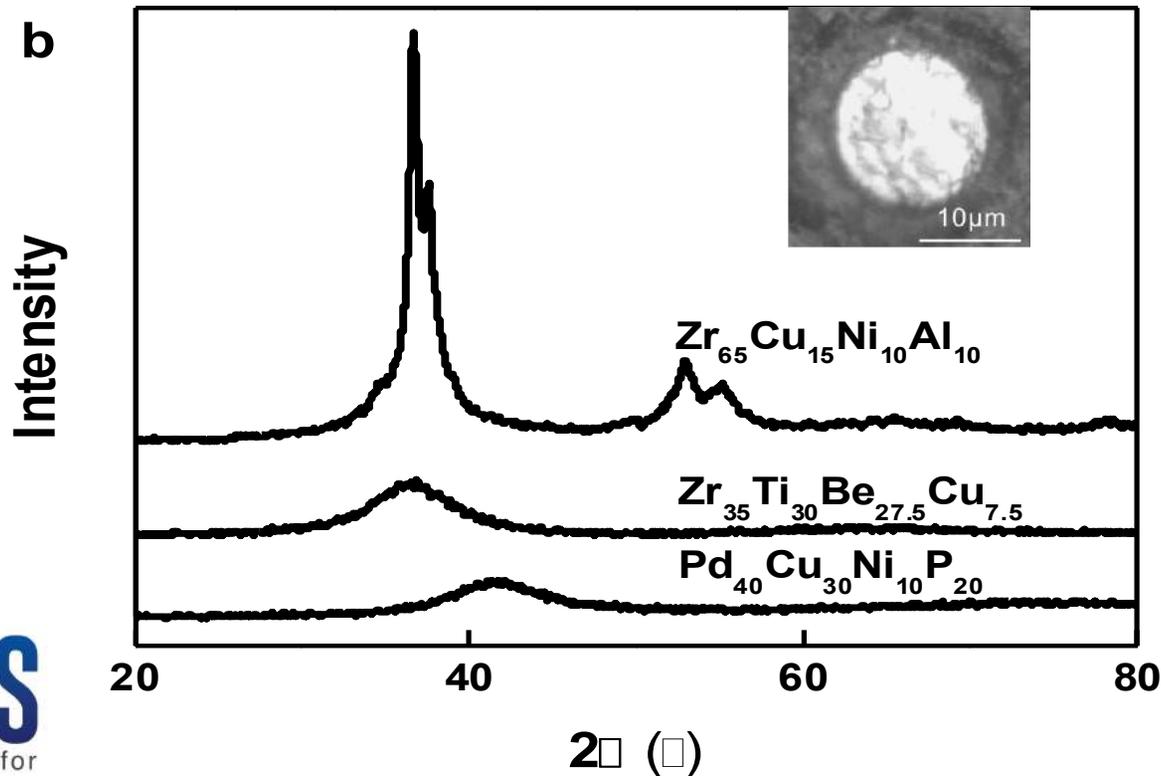
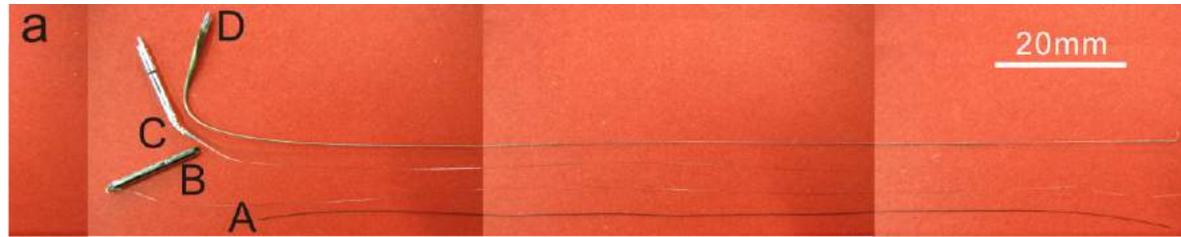
Macroscopic Appearance: Load Control

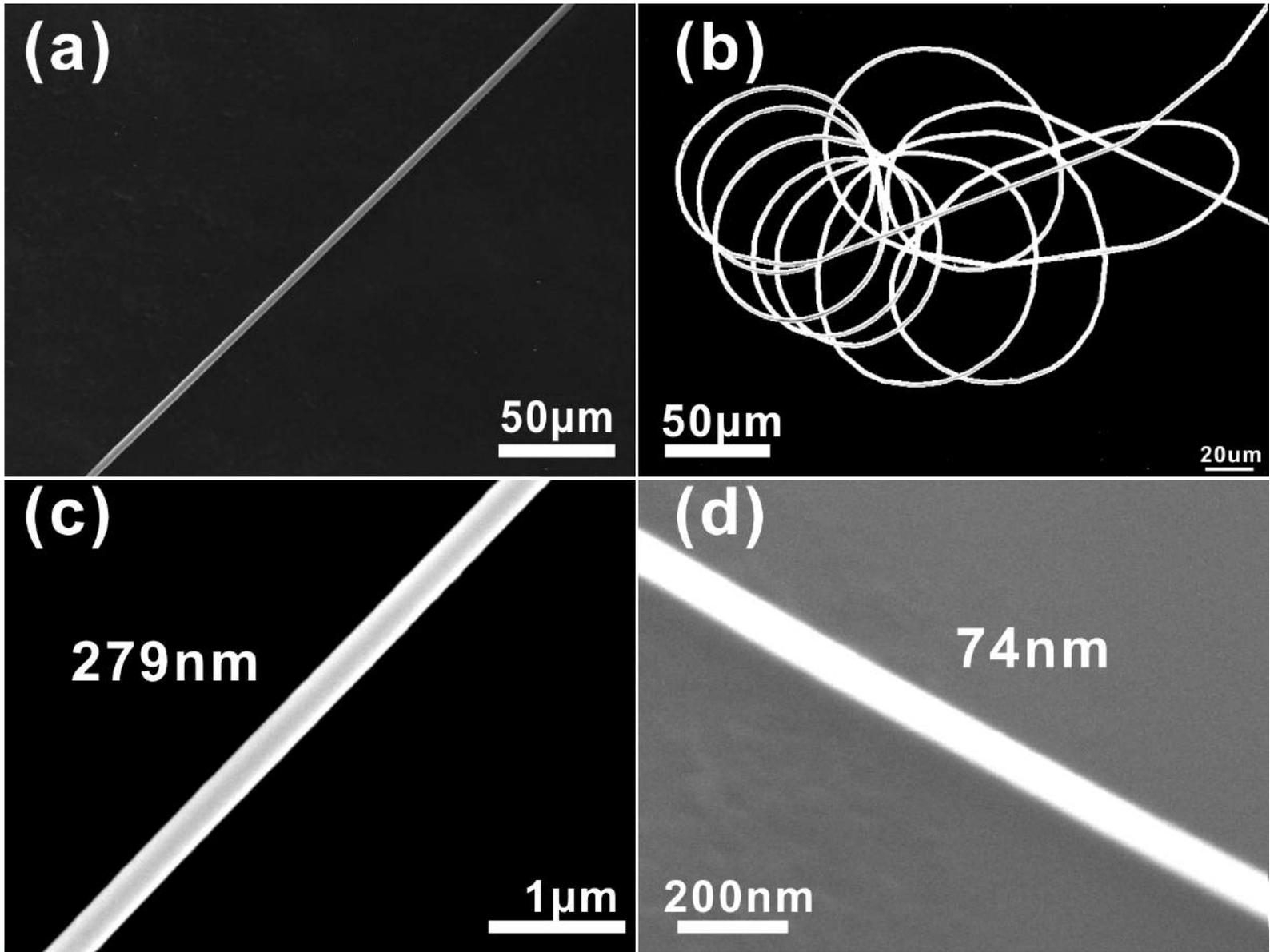
330° C		380° C			
0.34 lb/s	20 lb/s	0.34 lb/s	20 lb/s	200 lb/s	2000 lb/s
$8 \times 10^{-5} \text{ s}^{-1}$	$1 \times 10^{-3} \text{ s}^{-1}$	$2 \times 10^{-4} \text{ s}^{-1}$	$5 \times 10^{-3} \text{ s}^{-1}$	$2 \times 10^{-2} \text{ s}^{-1}$	$2 \times 10^{-1} \text{ s}^{-1}$
					

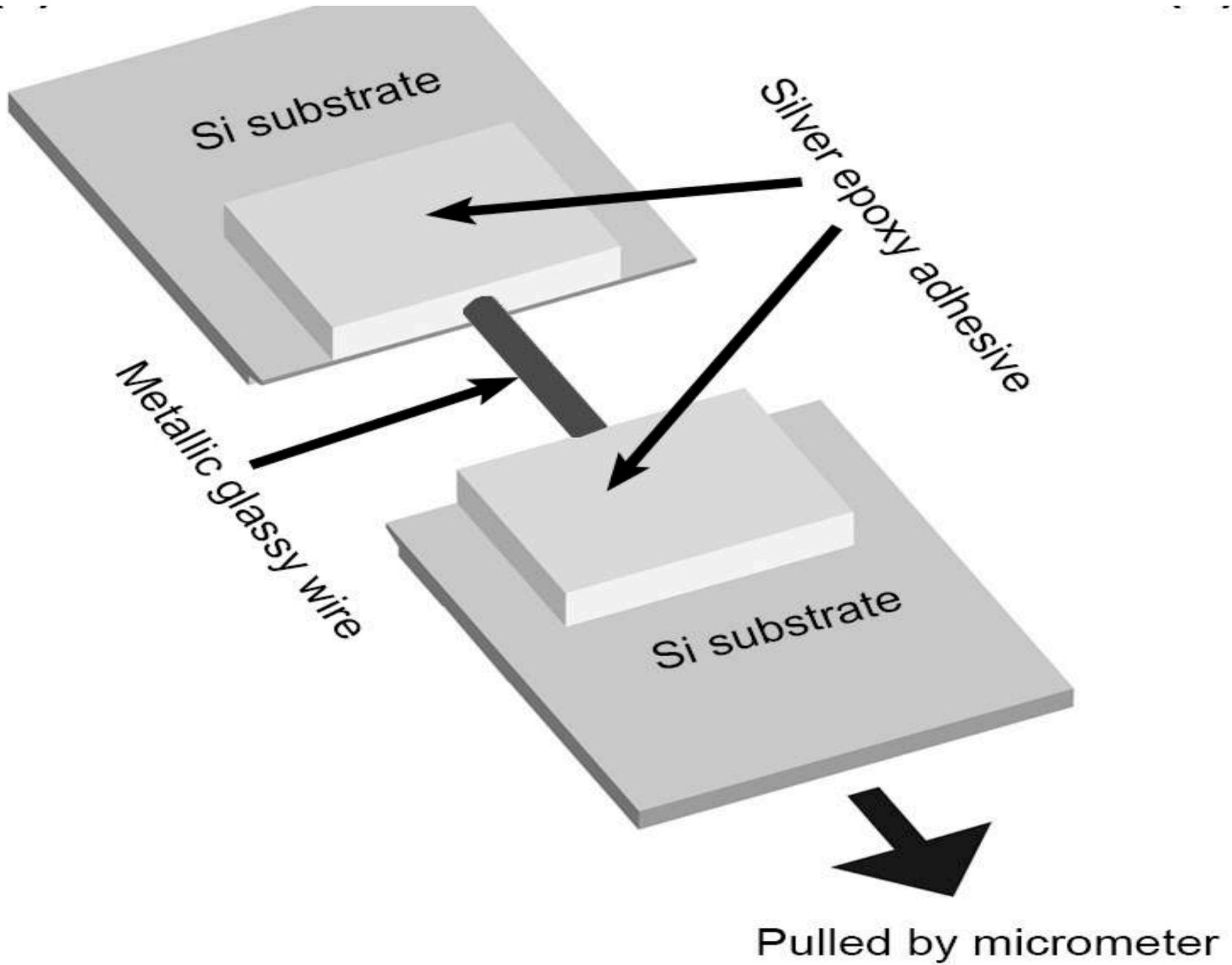
Fabrication of Metallic Glassy Wires



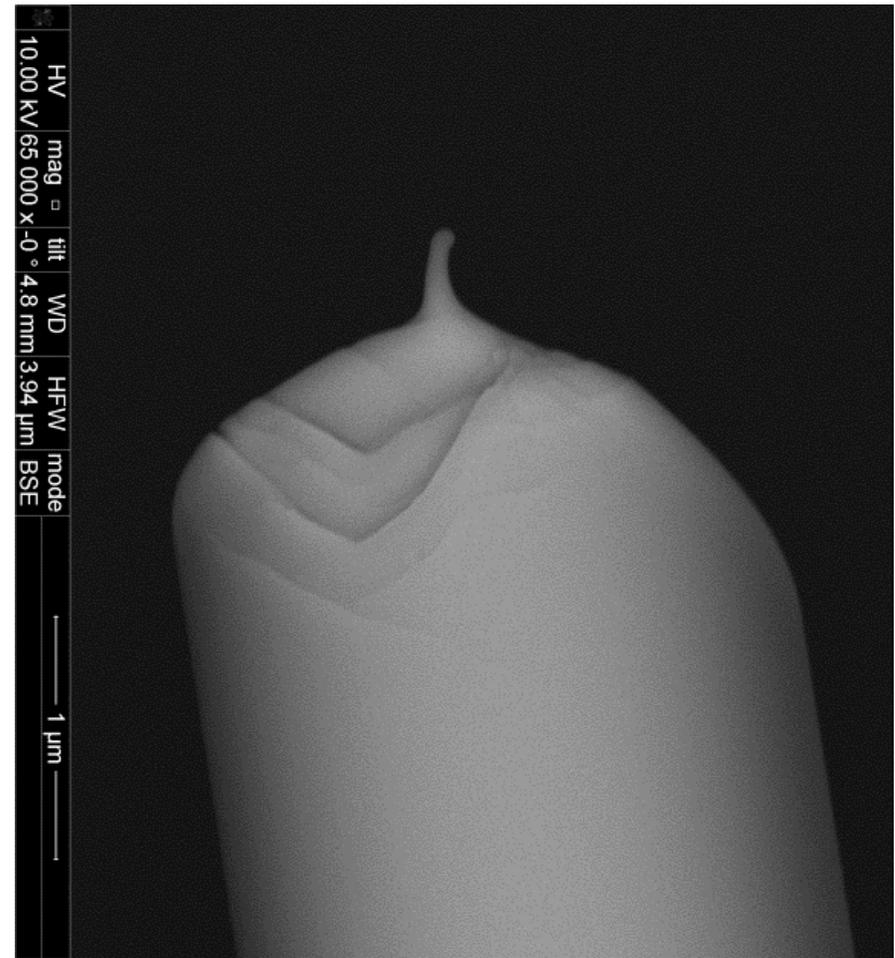
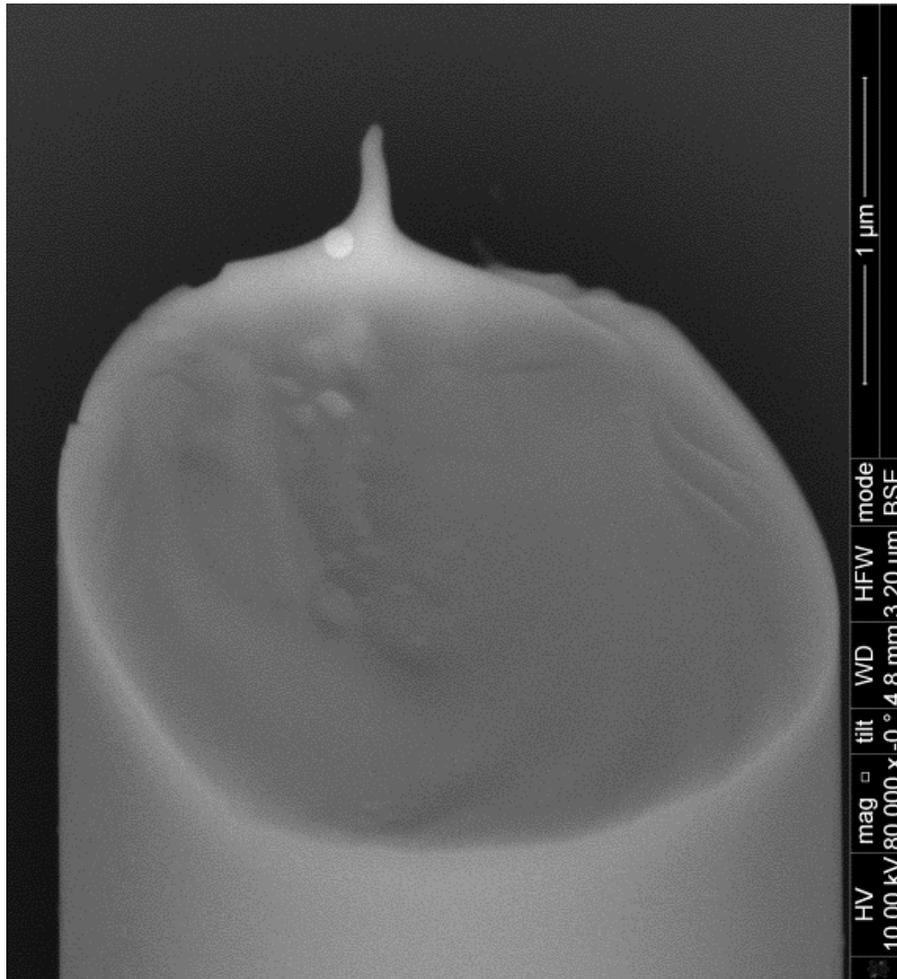
Appearance and Structure of Metallic Glassy Wires

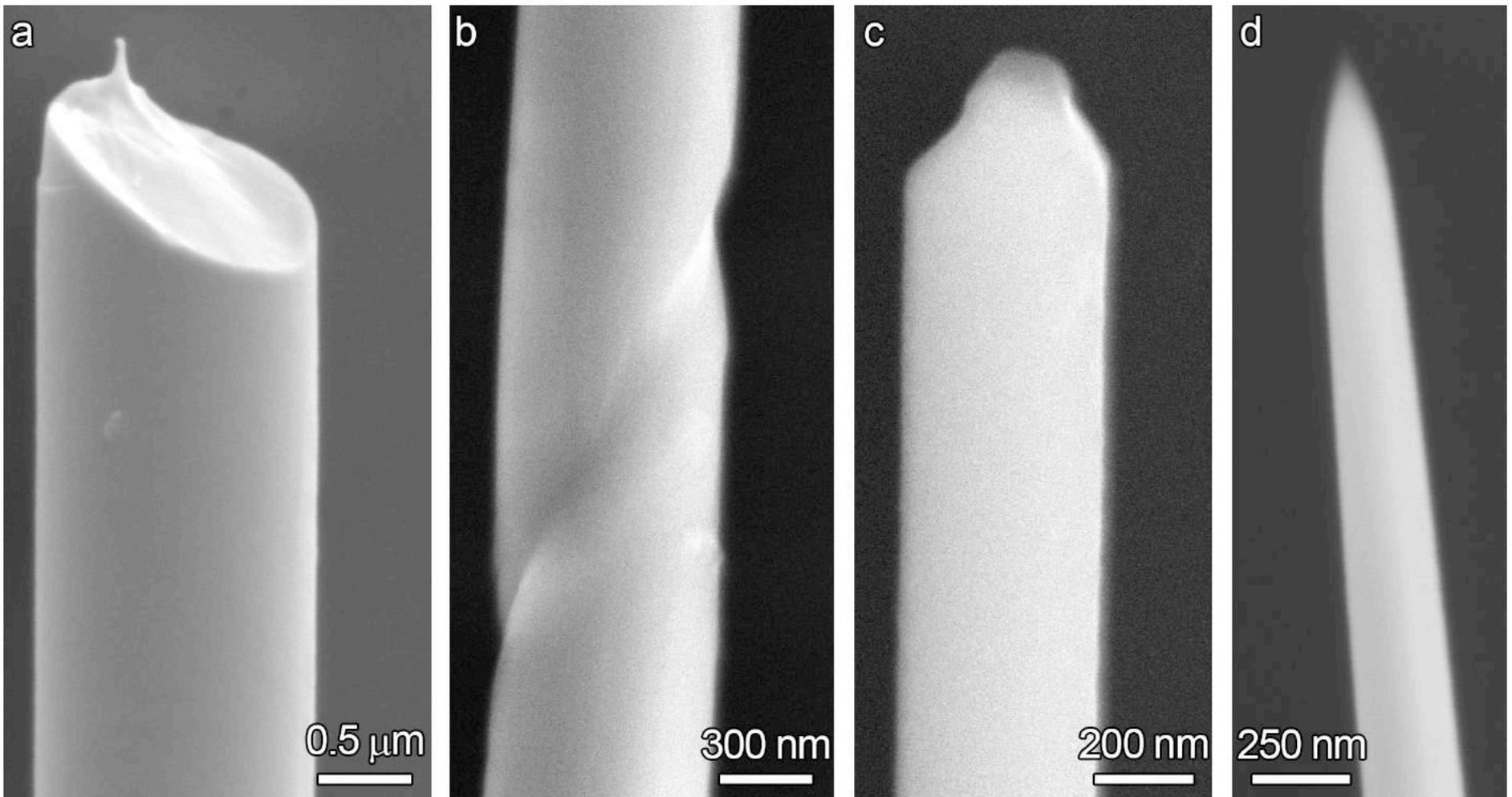






Tensile fracture surface of 1.48 μm $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ wire



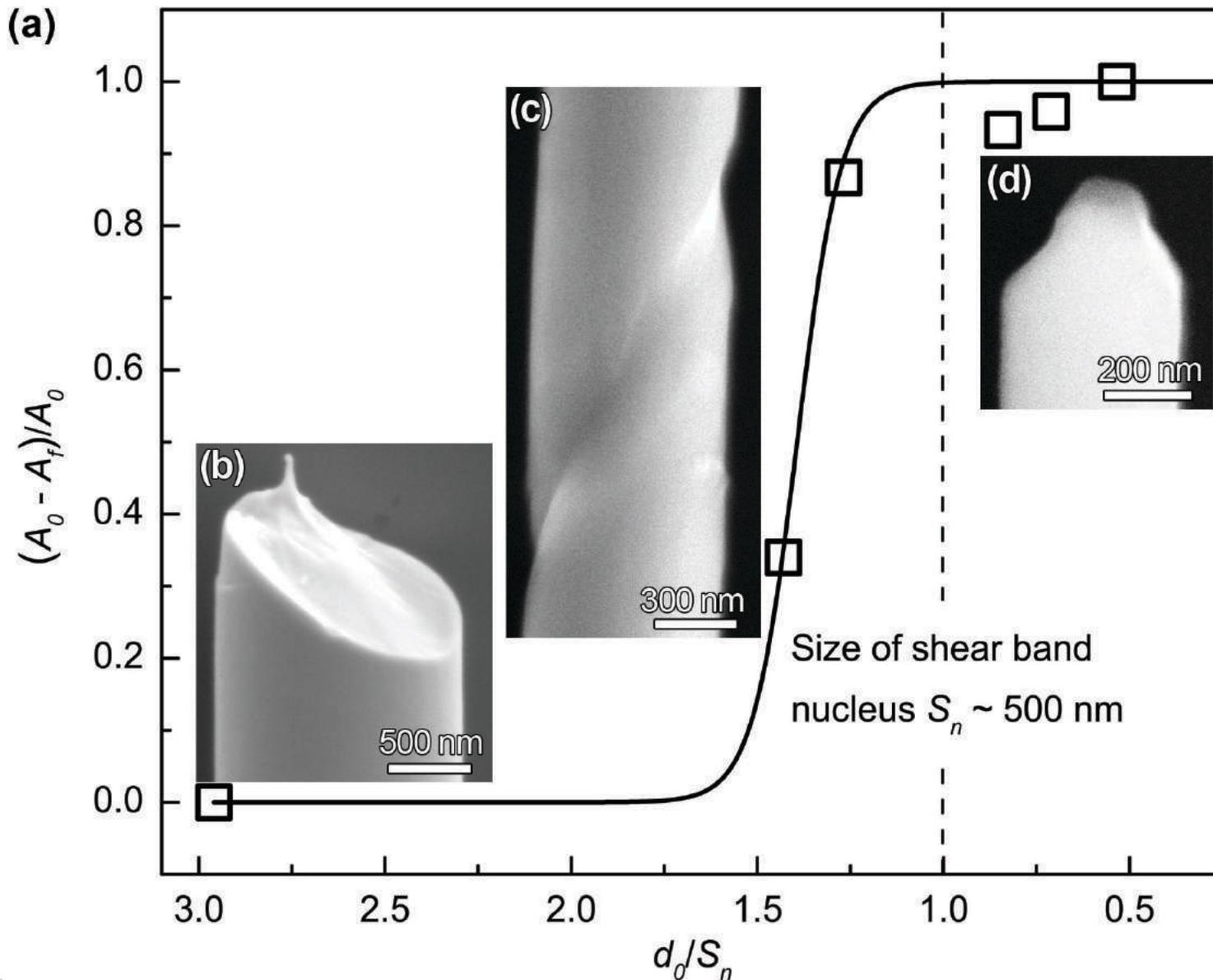


**Plasticity of 'Wires' Increases at Nano-scale!
No exposure to electron beam prior to tension test!**



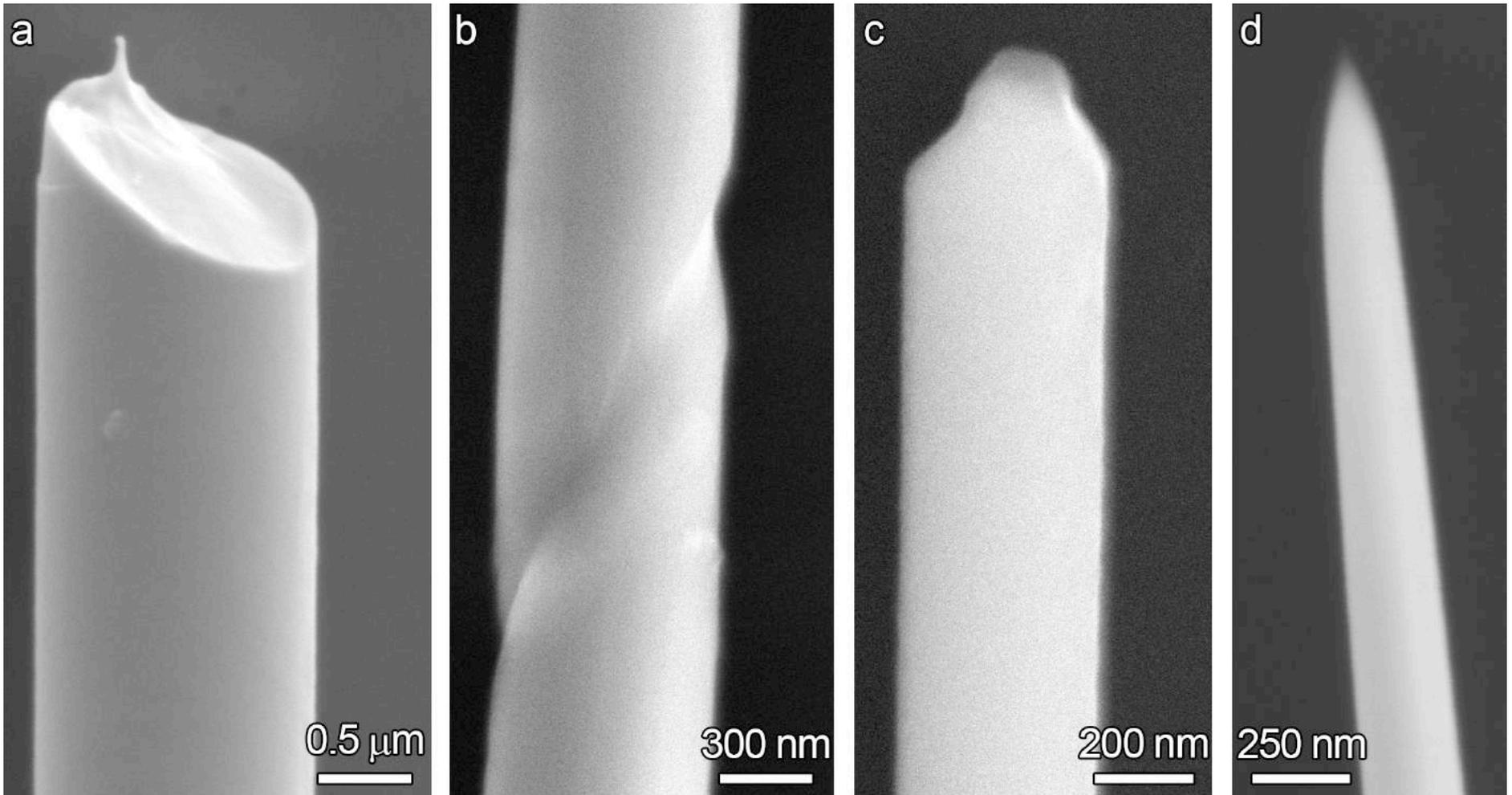
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Yi, Wang, Lewandowski *Acta Mater.*, 87, 1-7 (2015).



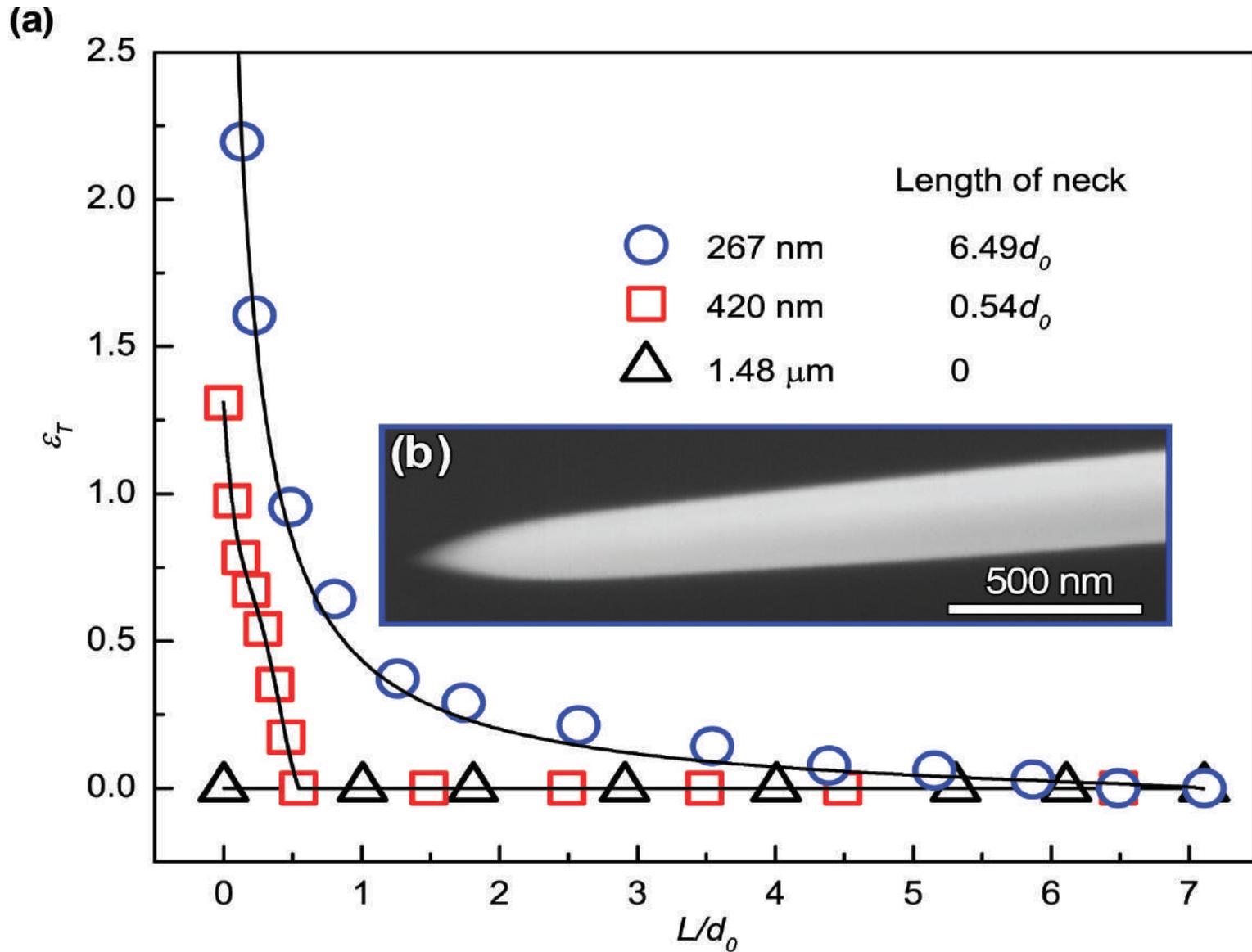
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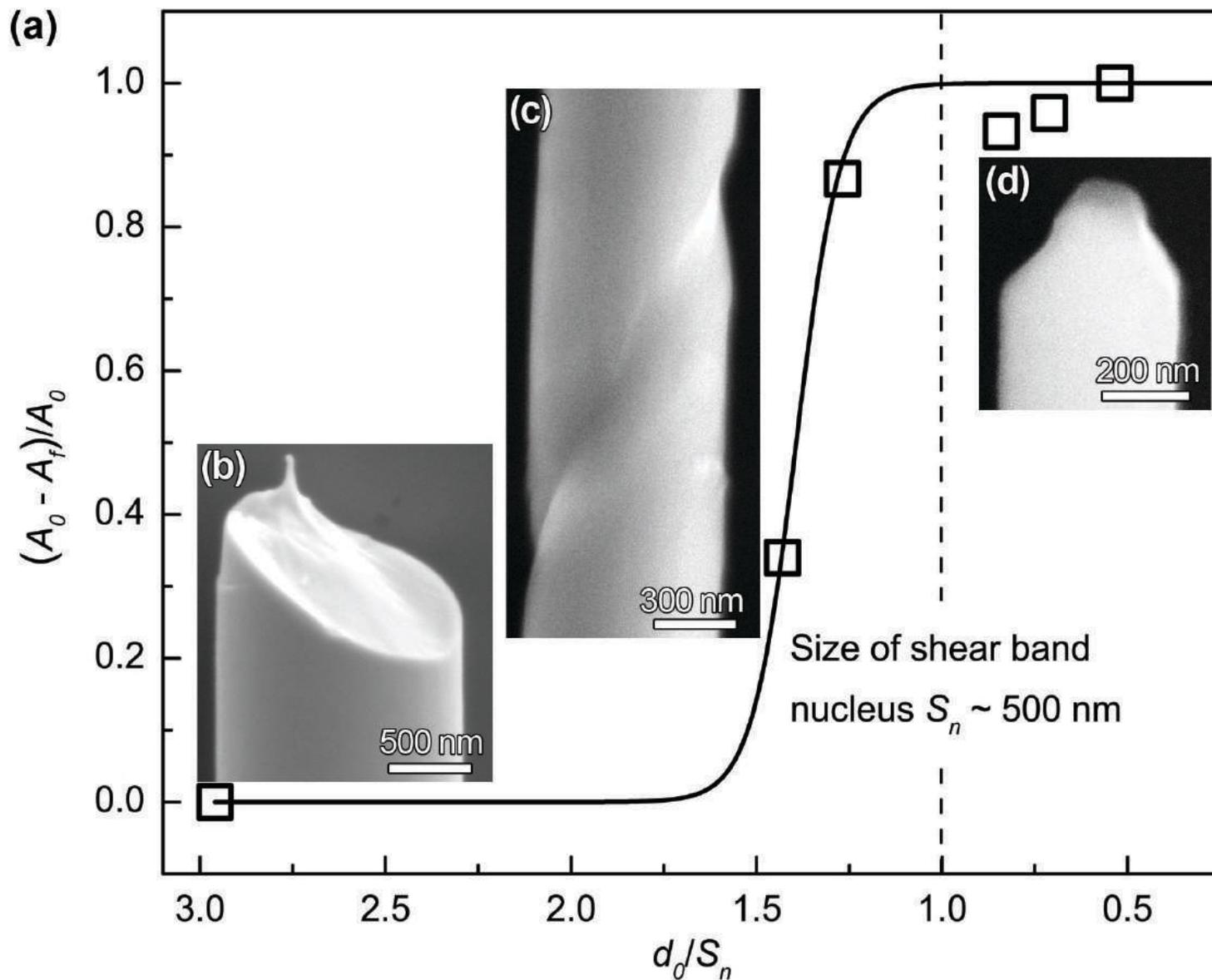
Shear Band Nucleus Size Estimate-Schuh et al, Acta Met, 2004
Yi, Wang and Lewandowski Acta Mater., 87, 1-7 (2015)



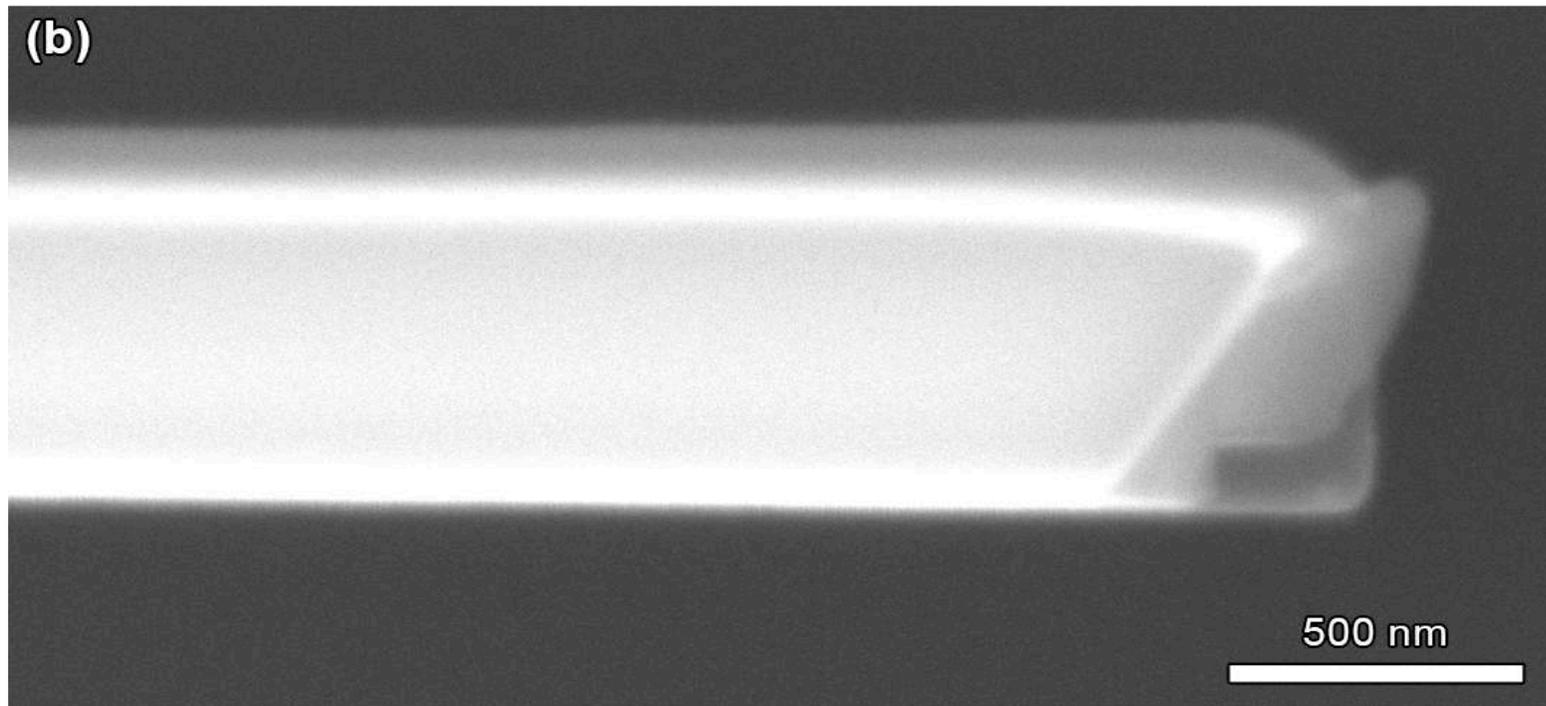
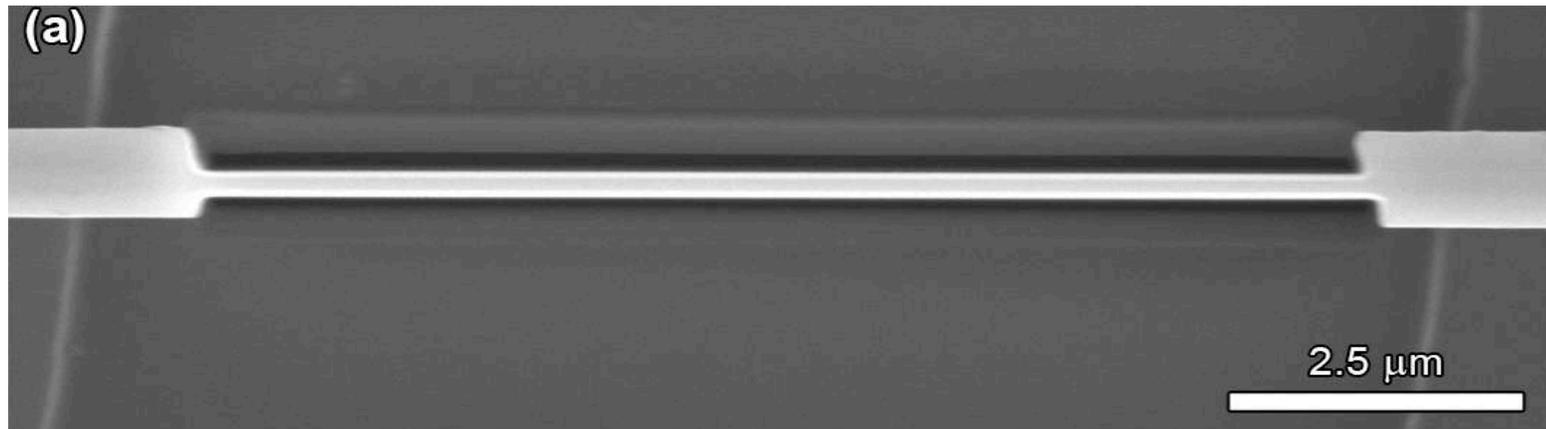
Quantify Strain Along Axis of Wire After Fracture

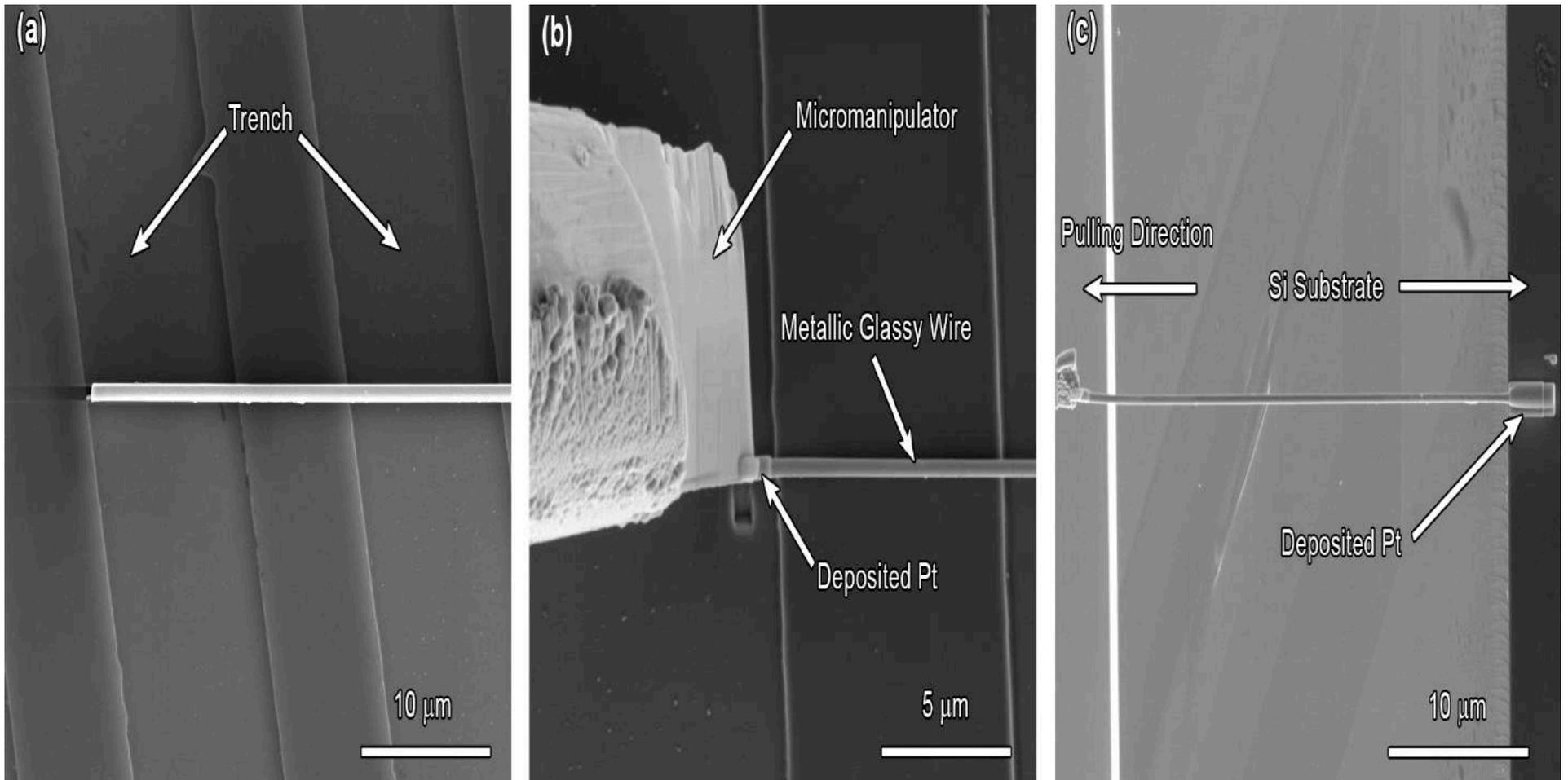
Yi, Wang and Lewandowski *Acta Mater.*, 87, 1-7 (2015)





Next: FIB large sample to smaller diameter (10 pA, 30 kV)
Will sample neck again or fail in shear?



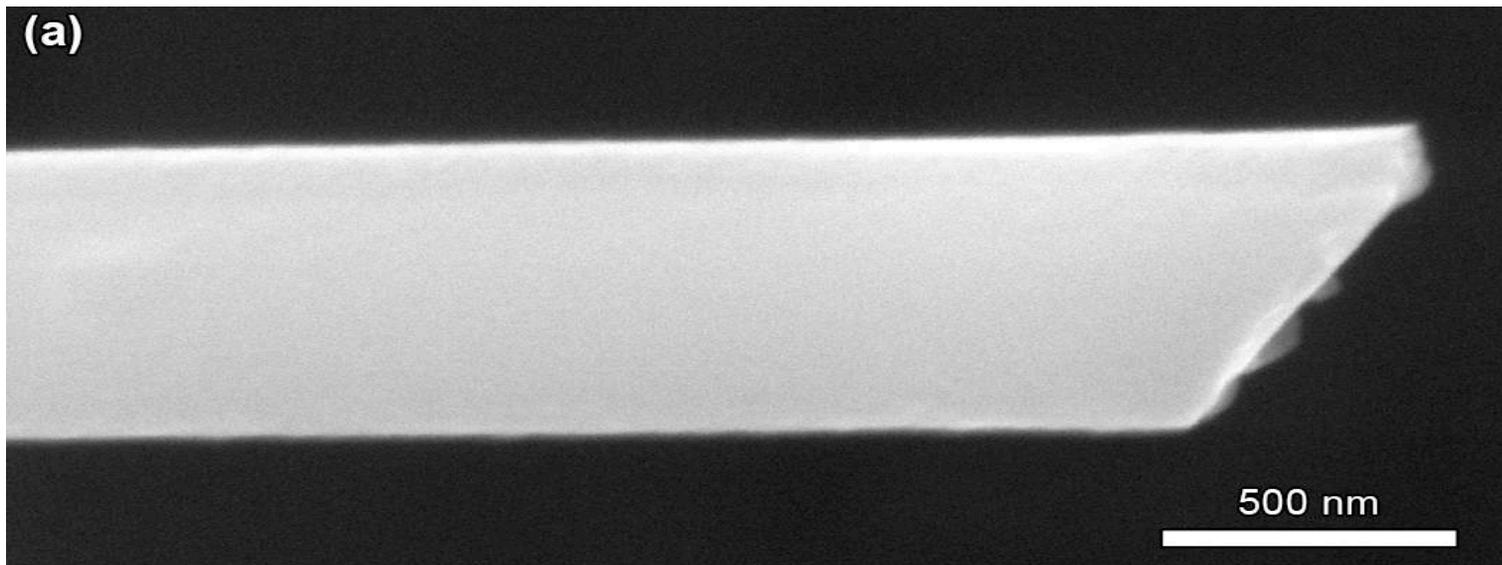


Next Set of Tests:

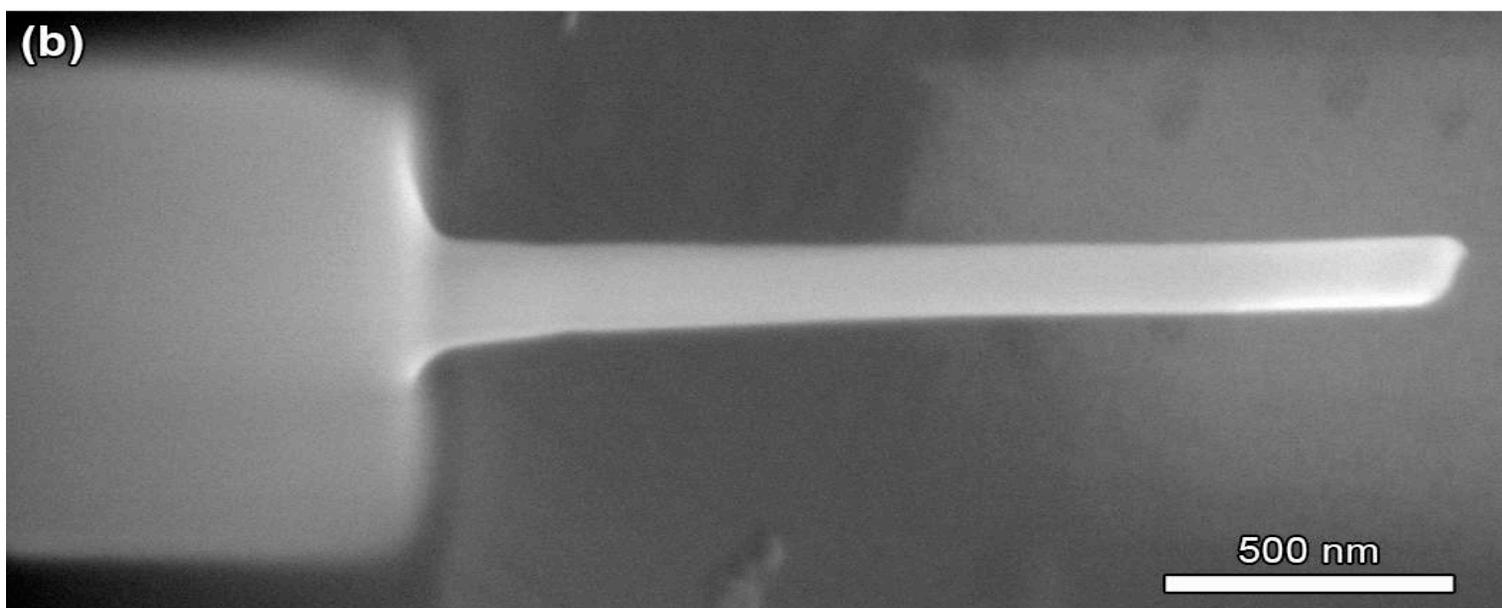
1. Utilize Pt-deposition to adhere to manipulator (10 pA, 30kV)
2. Cut via FIB
3. Transport and adhere via Pt-deposition to Si substrate
4. Ion Mill: 15kV, 4nA, 1 μm x 1 μm 10 sec
5. Pull to failure in tension with beam off



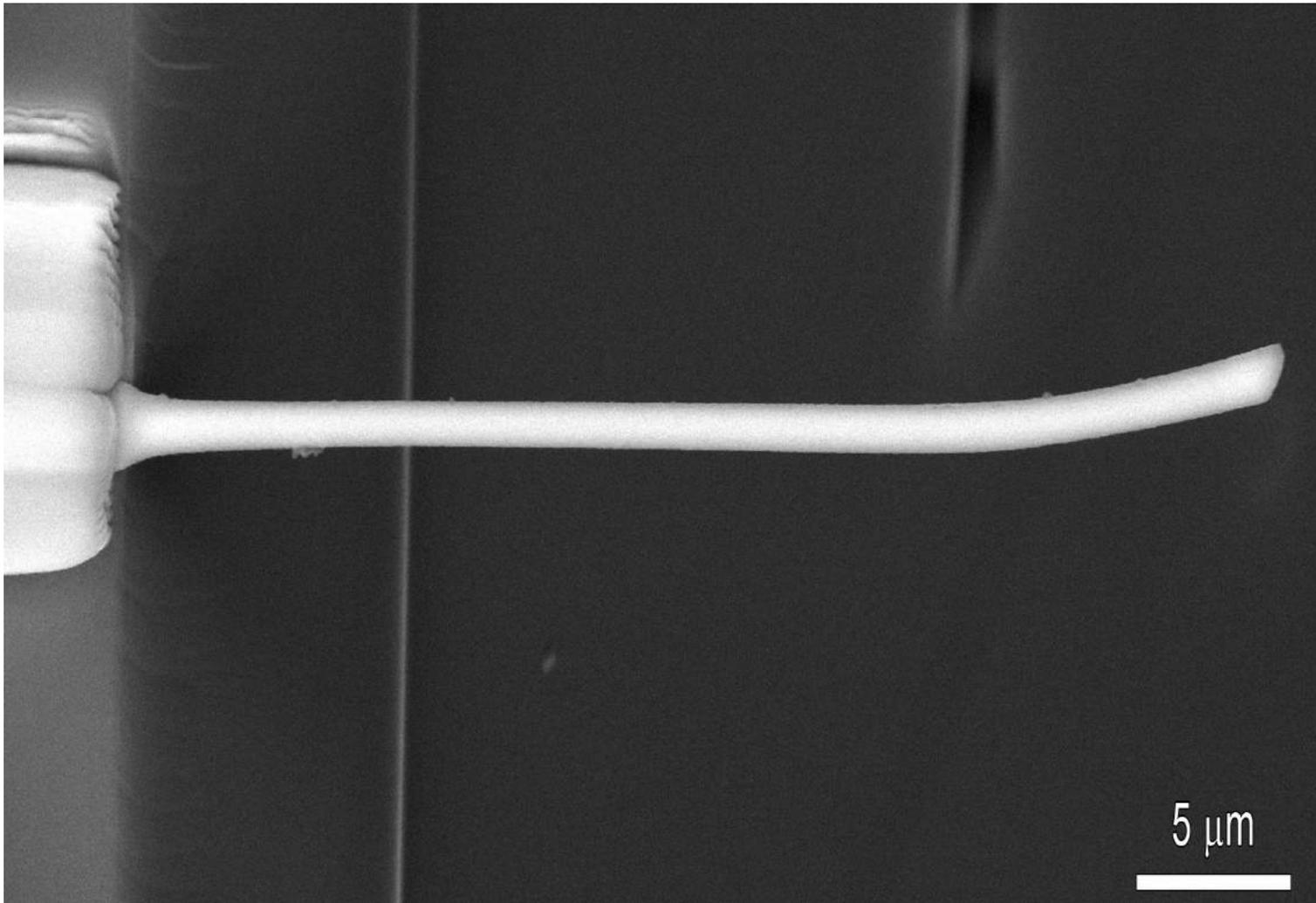
Yi, Wang and Lewandowski Acta Mater., 87, 1-7 (2015)



418 nm



150 nm



Pristine sample exposed to electron beam:

Bending in sample produced:

Artifacts can be introduced during preparation
and/or testing!

Yi, Wang and Lewandowski Acta Mater., 87, 1-7 (2015)



Summary

- **Size Effects on Plasticity**
 - **Fast Draw Method to Create Micro/Nano Wires**
 - **Initial Testing of Micro/Nano Wires**
 - **Size ↓, Plasticity ↑**
 - **Catastrophic Shear Transition to Ductile Rupture/Necking**
 - **Results Depend on Preparation/Test Technique**
 - **Damage introduced during sample preparation and/or testing changes results**
 - **Need to Determine Stress vs Strain Behavior to Extend Results**
- **Stress State Effects on Flow/Fracture of BMGs at RT ($T \ll T_g$)**
 - **Quick Review of Pressure Effects on Crystalline Metals**
 - **Minimal Effect of Superimposed Pressure on Strength/Plasticity**
- **Stress State and Temperature Effects on BMGs ($T \approx T_g$)**
 - **BIG Effects of Superimposed Pressure on Strength/Plasticity (Strength/Viscosity ↑↑, Plasticity ↓↓)**
 - **BIG Implications on Processing**
 - **Very Different than Crystalline Metals, More Similar to Polymers**



Outline

CWRU Activities Connected to Additive/Advanced Manufacturing

- ASTM F42 Definitions
- Example of Desire for Corrosion Resistant and Damage Tolerant Coating
 - Issues of Material Choice (Glass Forming, Damage Tolerant)
 - Thermal Stability, Microstructure Development, Properties
- America Makes/NAMII (National Additive Mfg Innovation Institute)
 - Powder Bed, Directed Energy Deposition (Laser Hot Wire)



Additive Manufacturing Categories

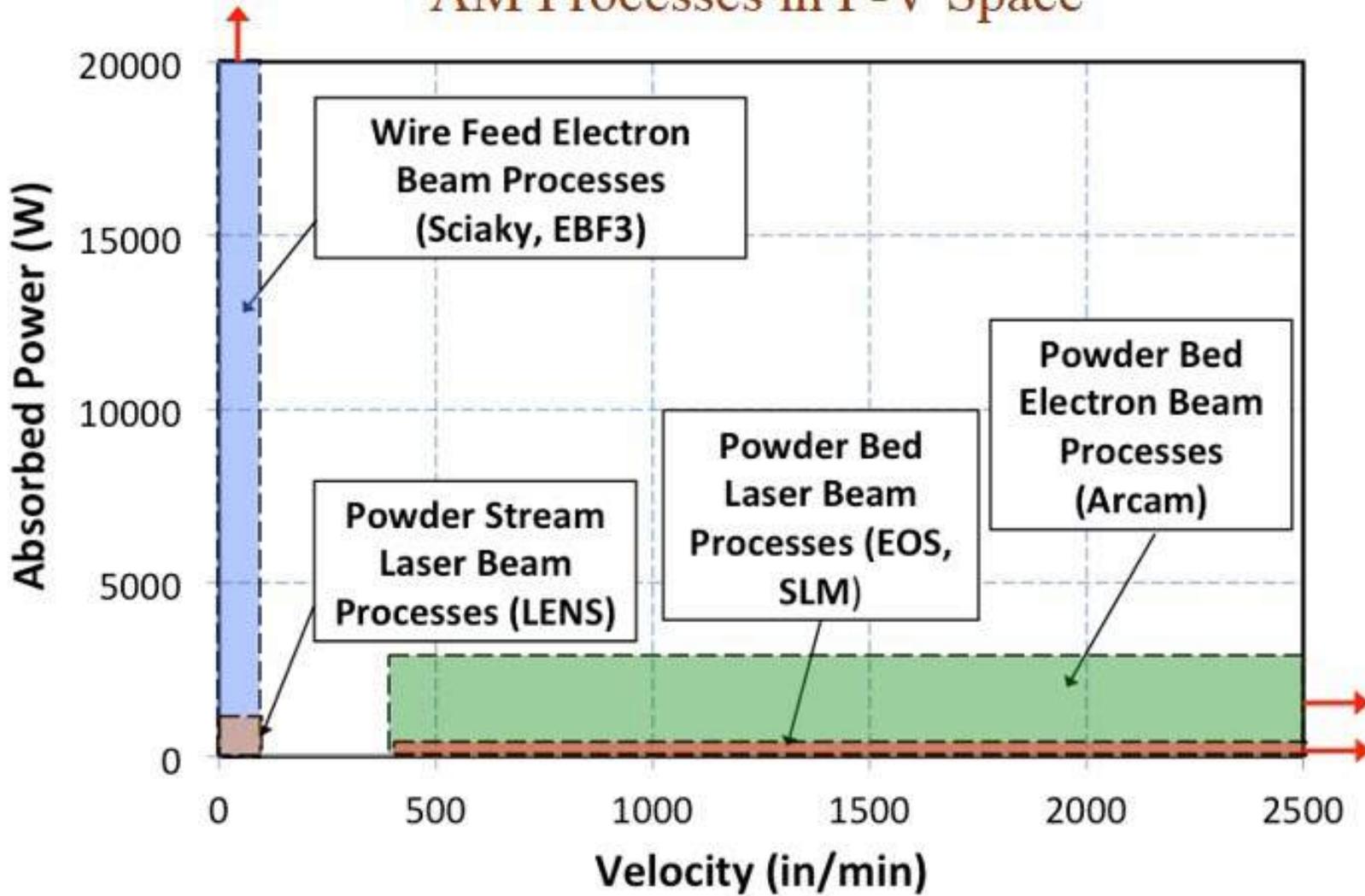
As defined by ASTM F42 Committee

Category	Description
Binder Jetting (Polymer/Metal/Other)	Liquid bonding agent selectively deposited to join powder
Material Jetting (Polymer)	Droplets of build materials selectively deposited
Powder Bed Fusion (Polymer/Metal)	Thermal energy selectively fuses regions of powder bed
Directed Energy Deposition (Metal)	Focused thermal energy soften/melts material as deposited
Sheet Lamination (Polymer/Metal)	Sheet of material bonded together
Vat Photopolymerization (Polymer)	Liquid photopolymer selectively cured by light activation
Material Extrusion (Polymer)	Material selectively dispensed through nozzle or orifice

Terminology Source: ASTM, Committee F42 on Additive Manufacturing Technologies



AM Processes in P-V Space



Development and Implementation of Metals Additive Manufacturing

Ian D. Harris, Ph. D.
Director, AMC
EWI, Columbus, OH

↑
Increased
Deposition
Rate

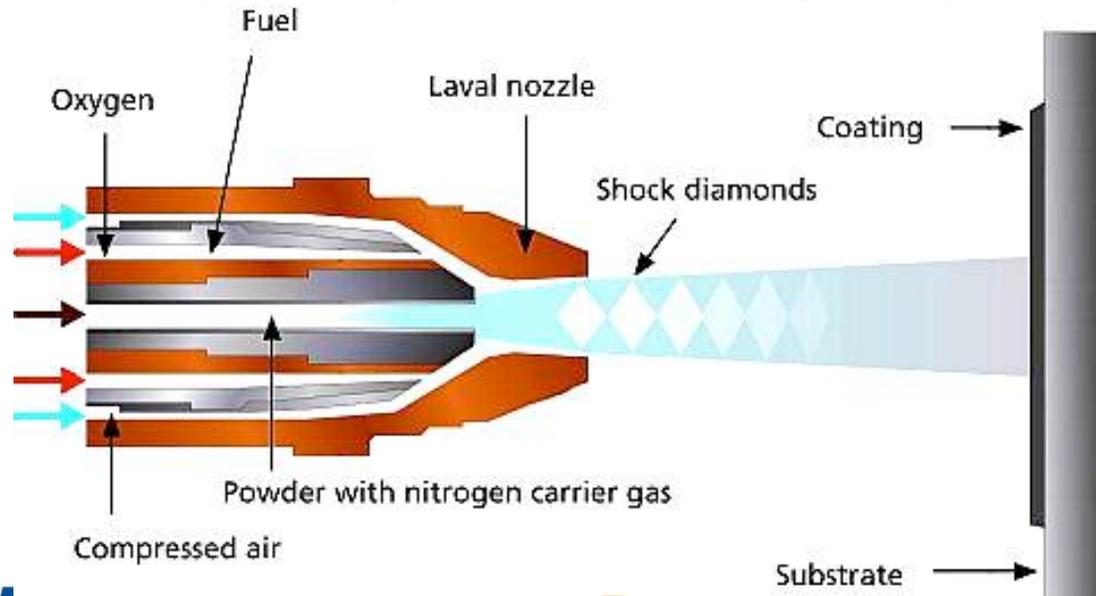


→ Decreased Resolution

➔ HVOF Coatings (Another High Deposition AM Process)

- ➔ Highly Dense, High Strength and Low Residual Tensile Stress or in Some Cases Compressive Stress
- ➔ Enables Much Thicker Coatings to be Applied than Previously Possible
- ➔ Amorphous Metal Powders
- ➔ High Kinetic Energy, No Molten Metal Needed

– *Need Properties of Metallic Glass as f (Temp., Time at Temp.)*



Sandia
National
Laboratories



Massachusetts Institute of Technology



CASE
CASE WESTERN RESERVE UNIVERSITY

UCDAVIS

Unique Flow Behavior as a f (Temperature)

Schematic of Deformation Map for a Metallic Glass

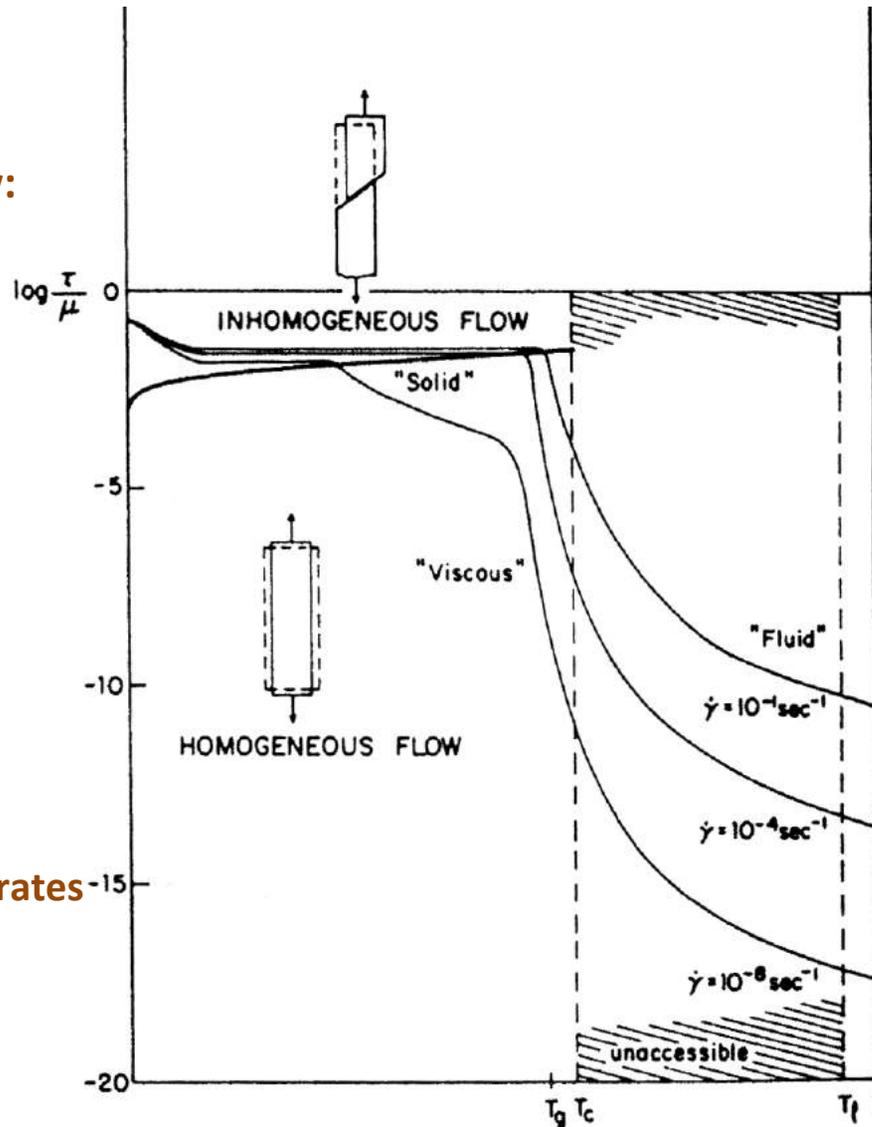
Inhomogeneous Flow:

- ➔ Shear Localization
- ➔ RT
- ➔ Near T_g at very high strain rates



Homogeneous Flow:

- ➔ Uniform deformation
- ➔ Near T_g at low and intermediate strain rates



Spaepen F. , *Acta Metall.* 25 (1977) 407-415.

Materials & Experimental Procedures:

➔ Materials used:

➔ $\text{Fe}_{48}\text{Mo}_{14}\text{Cr}_{15}\text{Y}_2\text{C}_{15}\text{B}_6$ (Drop-Cast Ingots, ORNL ; 5 mm dia. X 75 mm long)

— T_g : 560-575°C T_x : 623°C

(Perepezko, et al., Intermetallics (2006) 14, 898)

➔ Hastelloy® Alloy C-22

➔ Stainless Steel 316L

➔ Instruments :

➔ High Temperature Micro-Hardness Tester

— Nikon QM

➔ XRD

— Scintag X1 apparatus using Cu-K α radiation

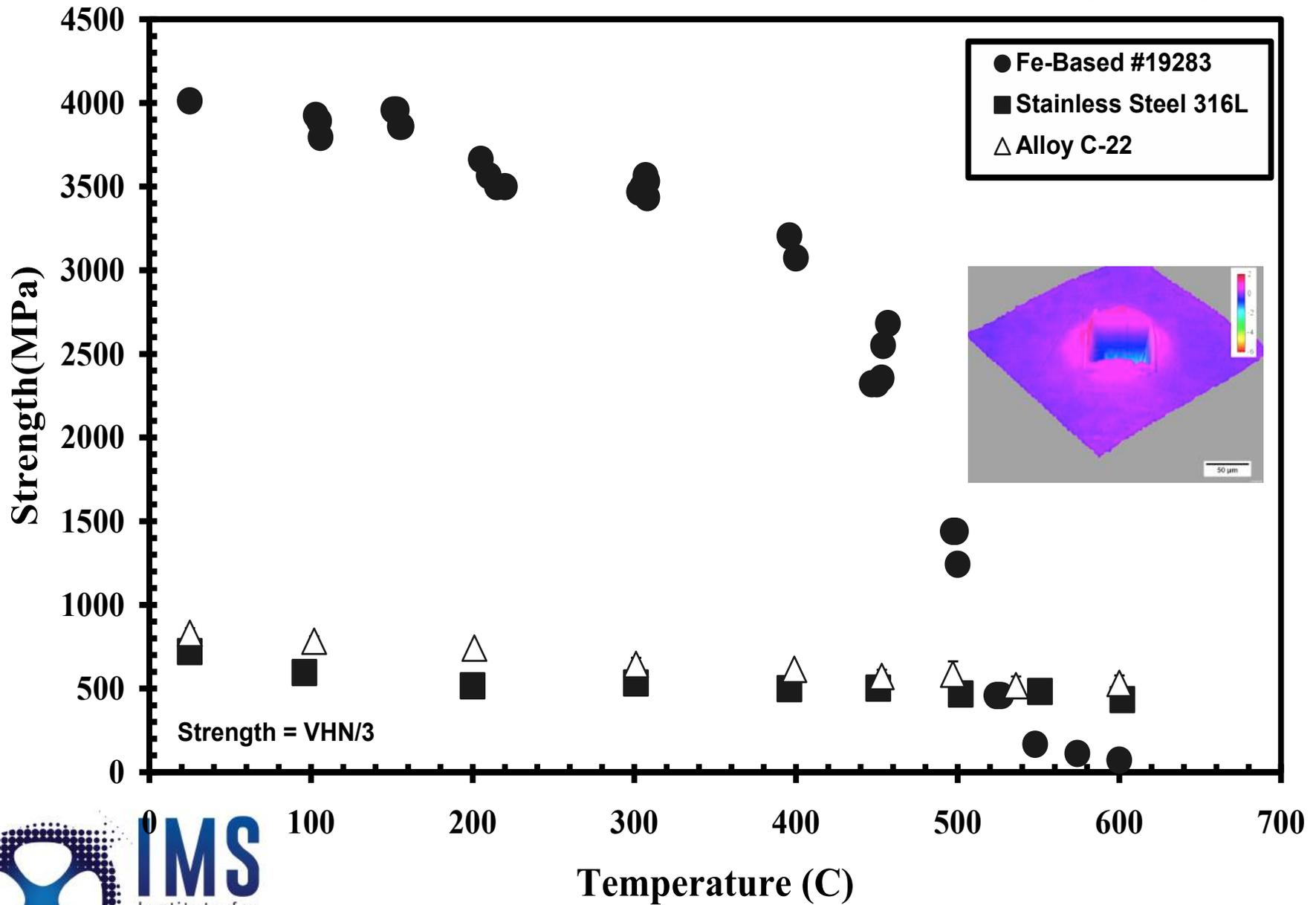
➔ TEM

— JEOL 2010 FasTEM, operating at 200kV



A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

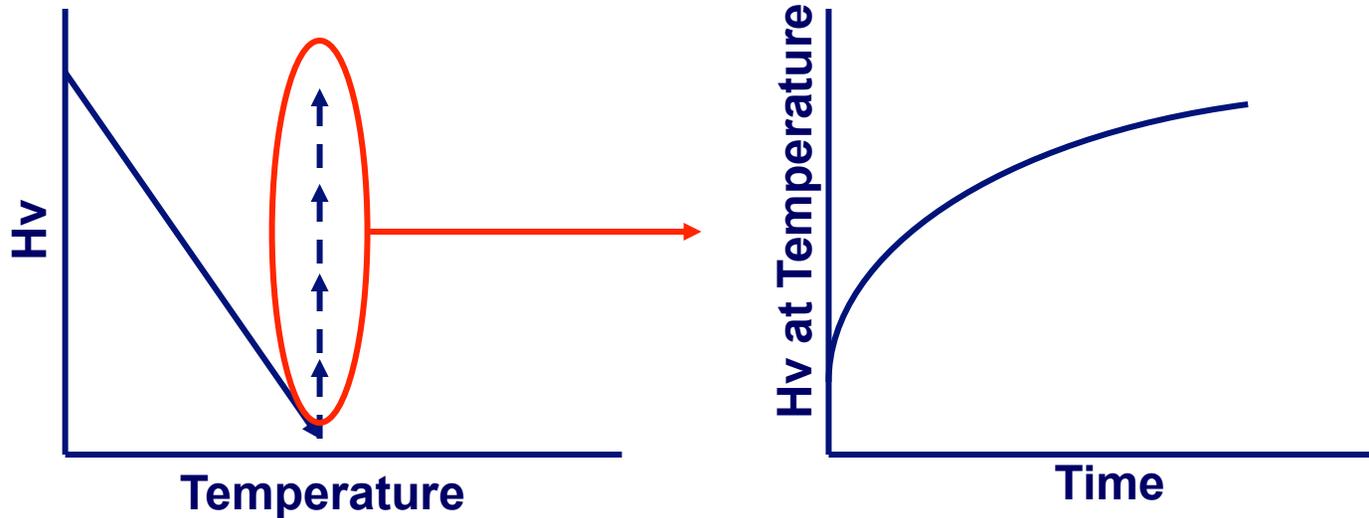
Strength vs. Temperature of $\text{Fe}_{48}\text{Mo}_{14}\text{Cr}_{15}\text{Y}_2\text{C}_{15}\text{B}_6$



A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

Experimental Procedures: Thermal Exposure Effects

→ Hv Evolution vs. Time at Temperature



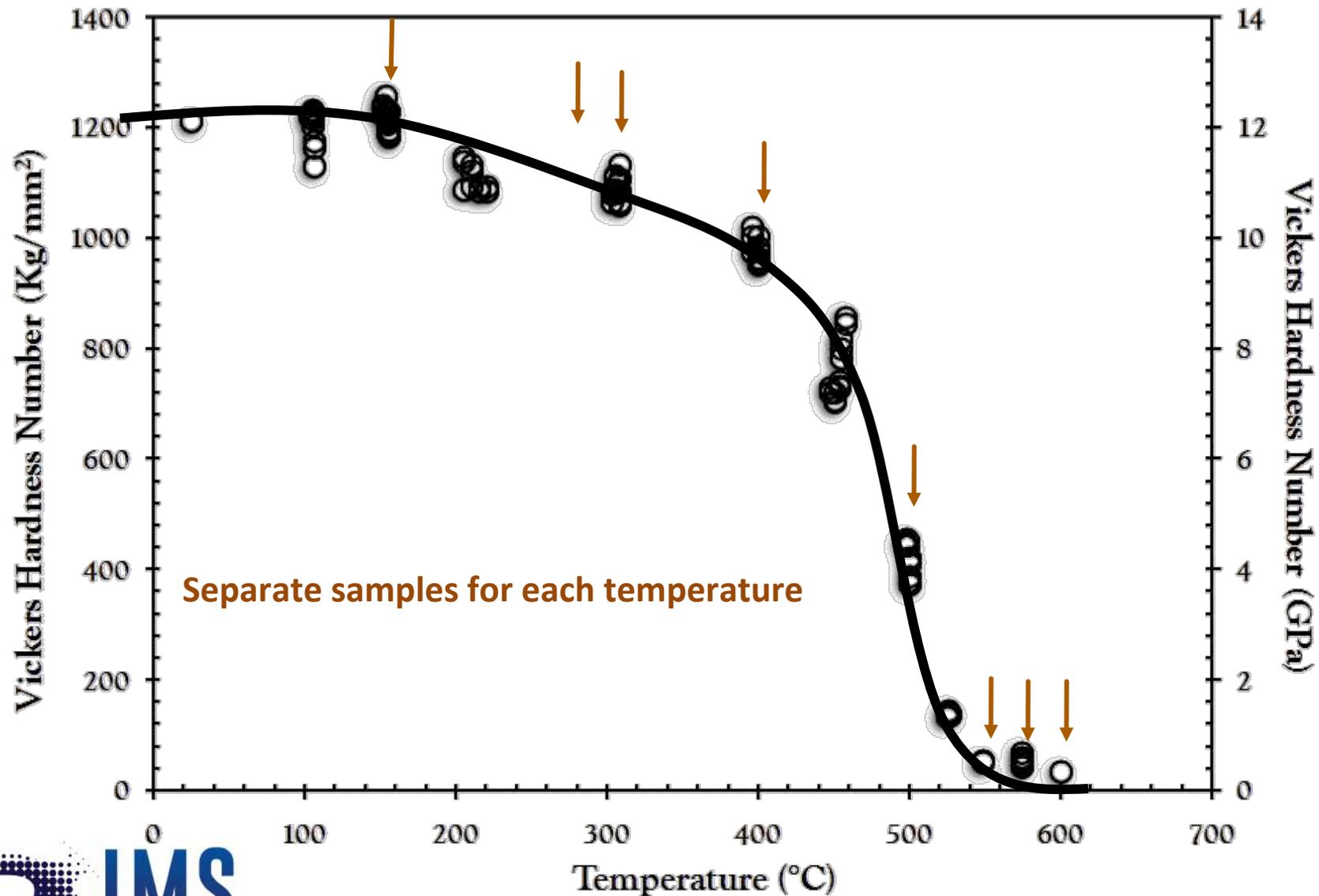
— Temperatures Chosen:

150°C, 275°C, 300°C, 400°C, 500°C, 575°C, 600°C, 620°C



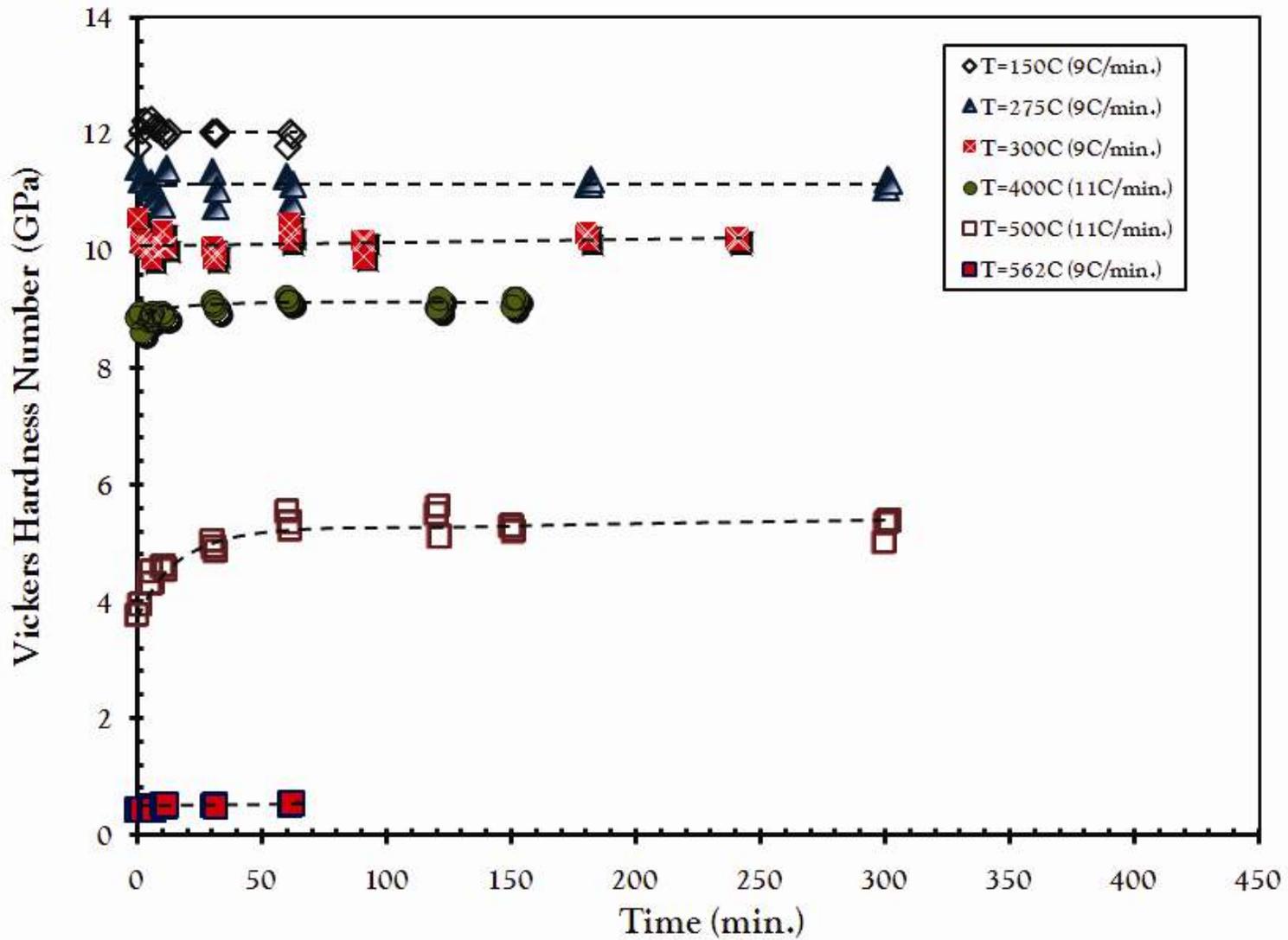
A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

Temperatures for Hardness Evolution Studies

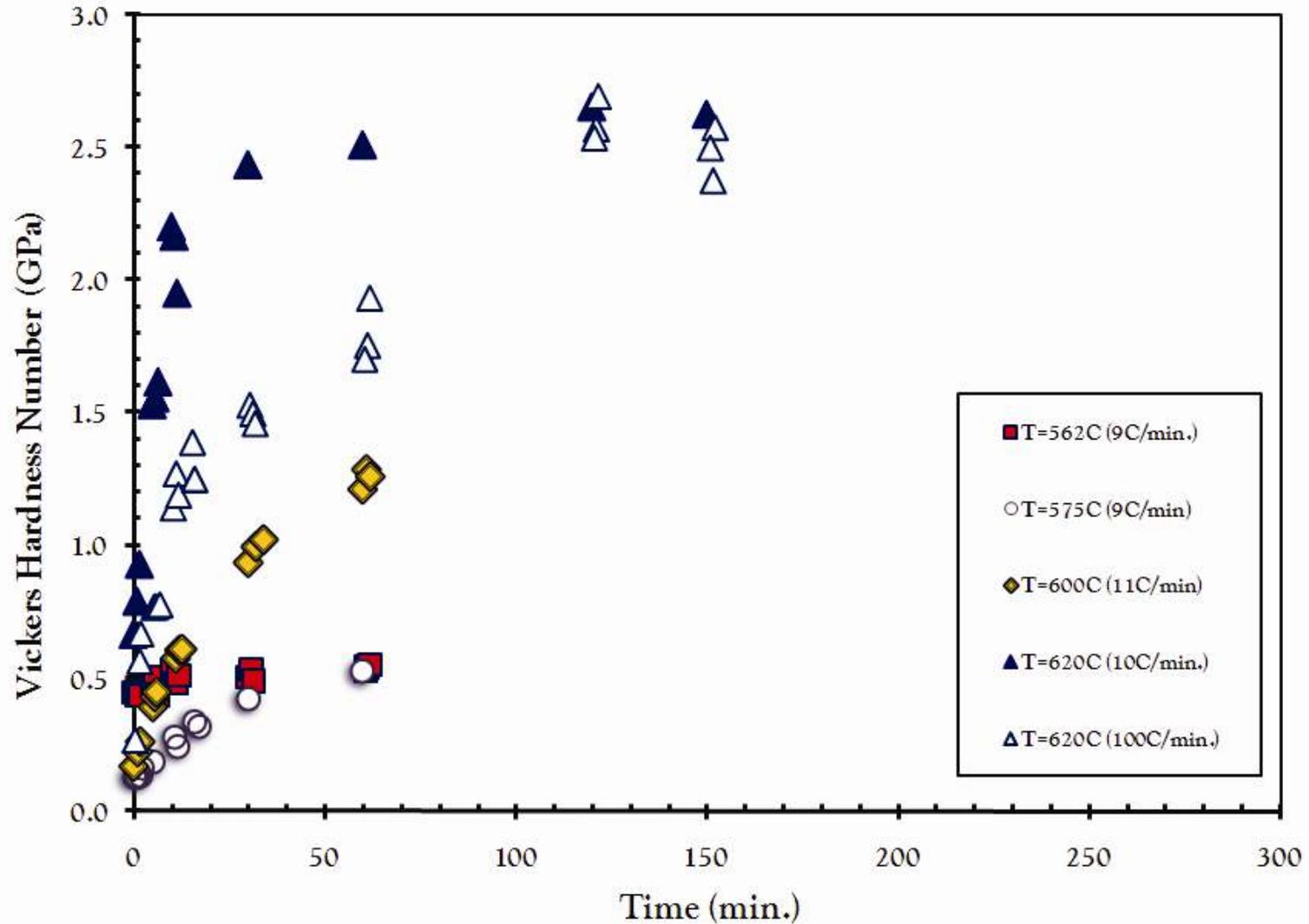


A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

Vickers Hardness vs. Time – $T < T_g$



Vickers Hardness vs. Time – $T \approx T_g$



A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

TEM Studies: Conventional & *In-situ*

➔ TEM Experiments: (Yi Liu, Wayne State University)

➔ Conventional TEM

- ➔ Performed on thermally-exposed samples from hardness test

➔ *In-situ* TEM

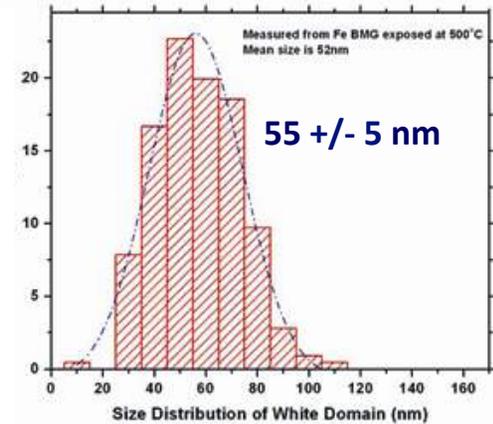
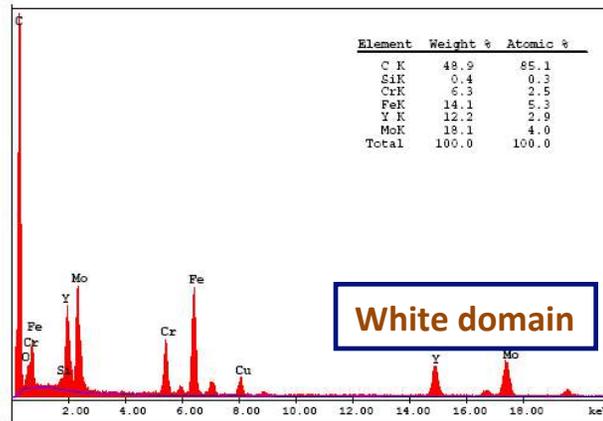
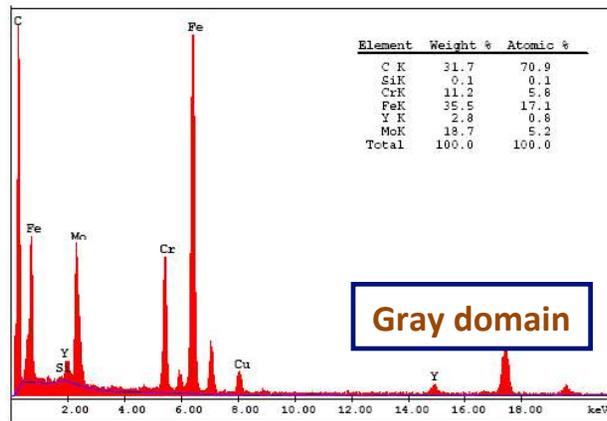
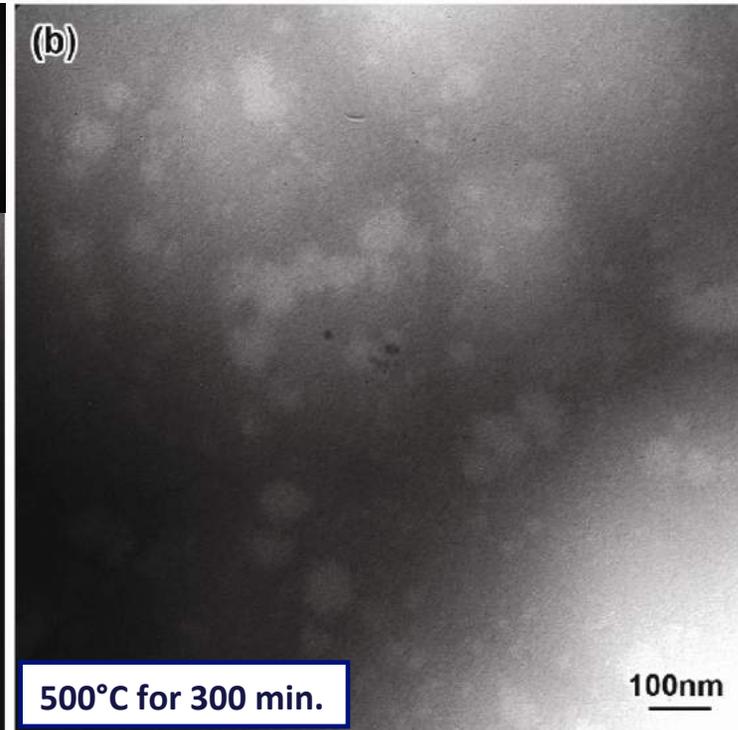
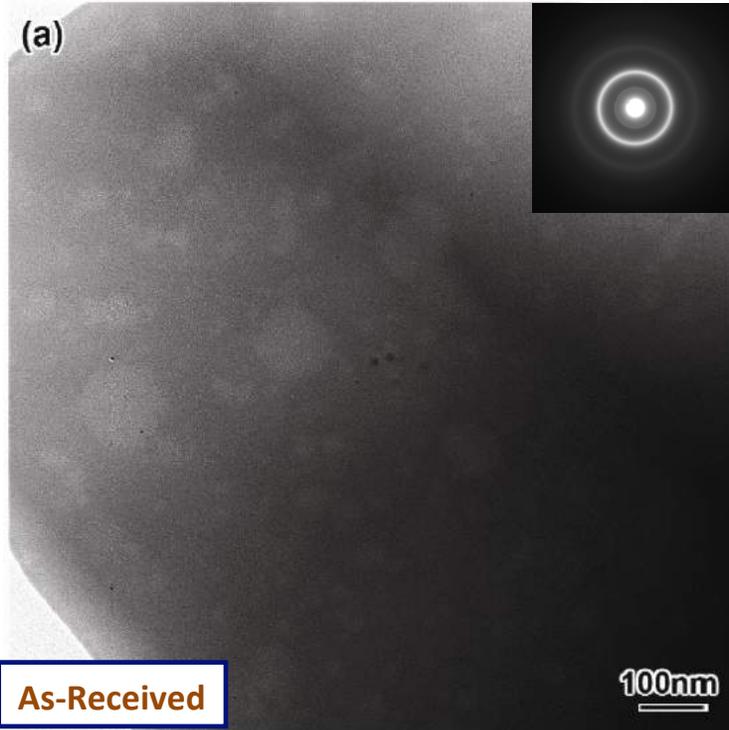
- ➔ crystallization/structure evolution as a function of temperature
- ➔ crystallization/structure evolution as a function of time at temperature
 - ➔ Separate samples for temp./time combinations

➔ TEM Sample Preparation:

- ➔ Samples were sliced to 0.5-0.8mm thickness
- ➔ Ground to 50 μ m thickness using dimpling grinder
- ➔ Gatan ion beam milling at 5kV (5 degrees angle) at room temperature



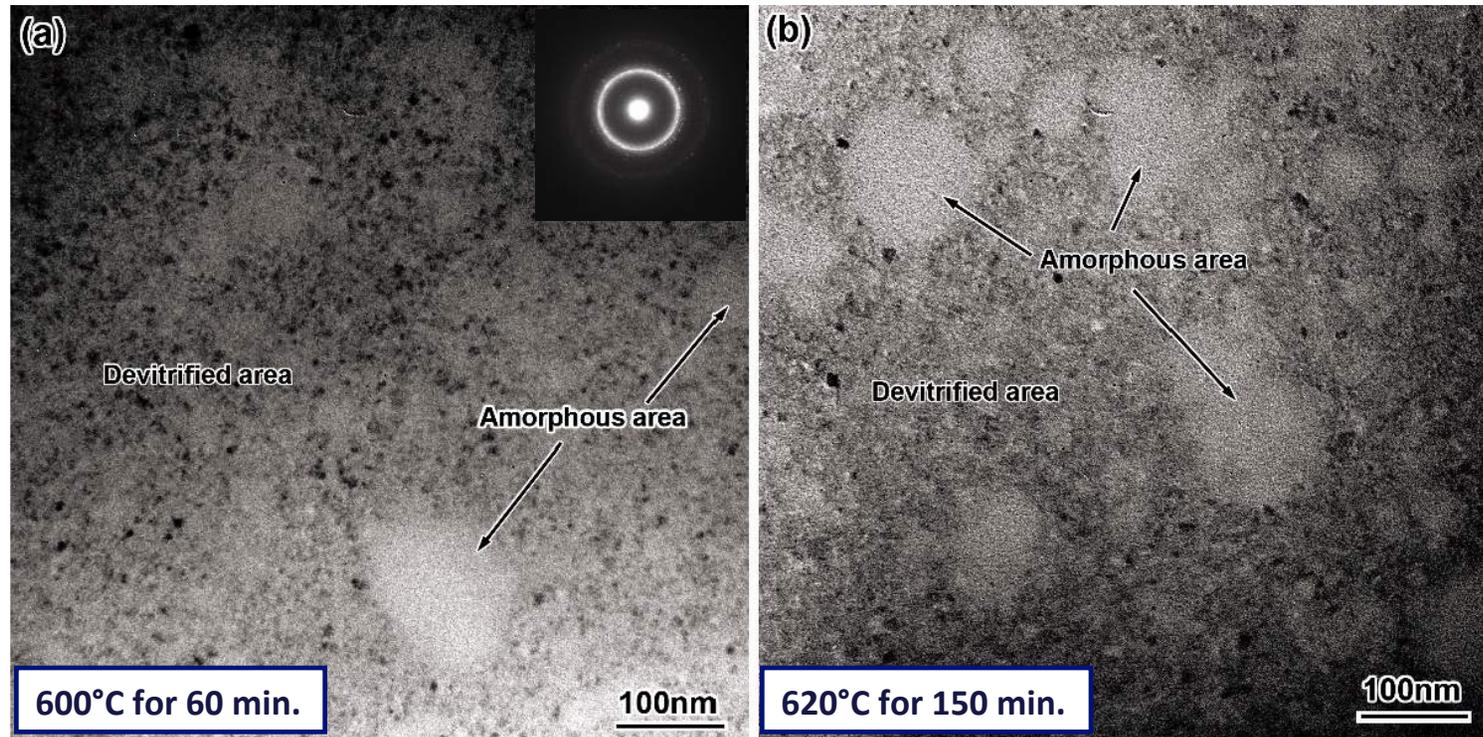
Conventional TEM



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A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

Conventional TEM



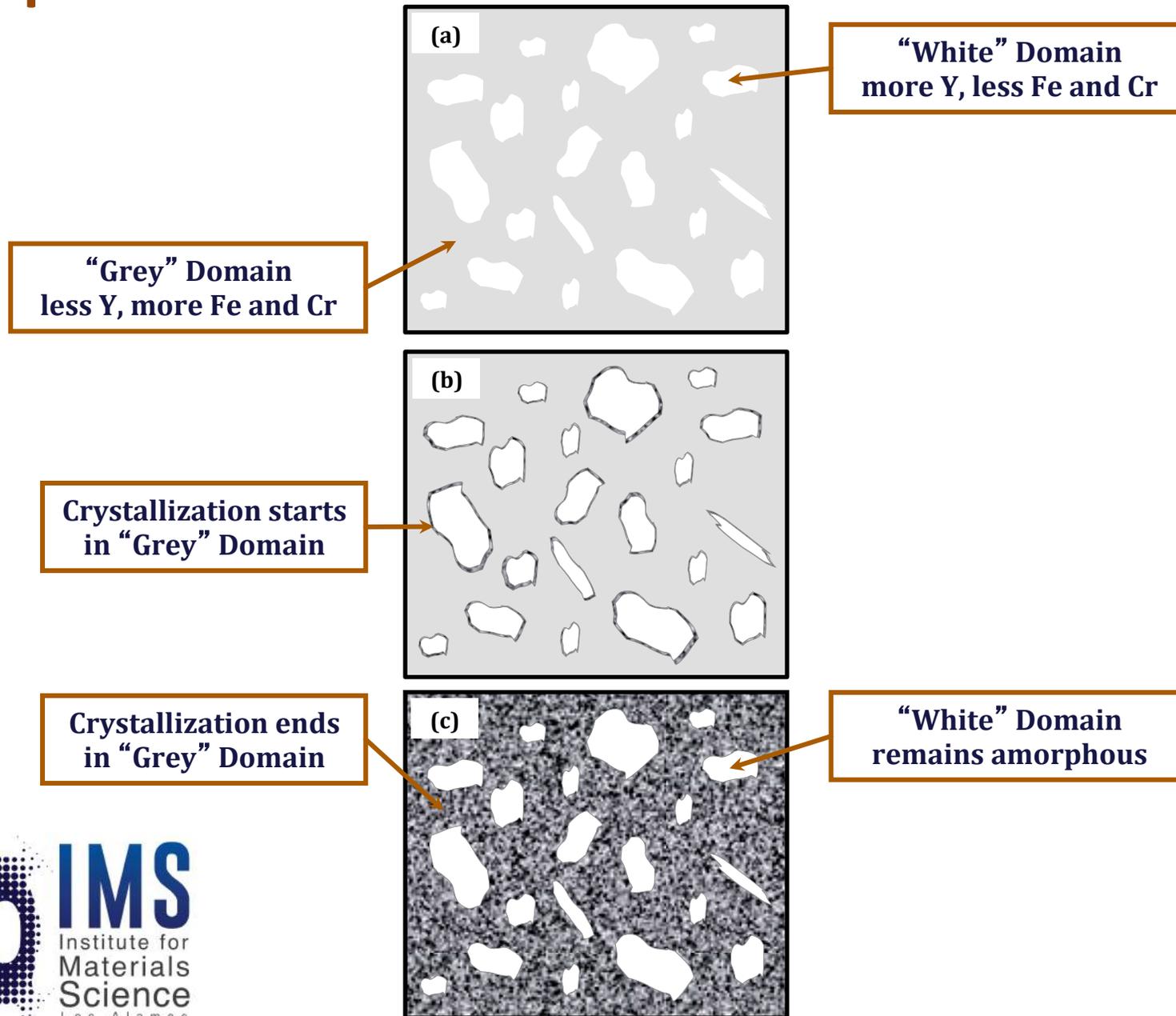
Sample	Fe		Mo		Cr		Y	
	Gray Domain	White Domain						
As-received	17.1	5.3	4.9	4	5.7	2.5	0.7	2.9
500 °C/300 min	27.4	12.2	7.7	6.8	8.9	5.2	1	4.5
620 °C/150 min	43.5	21.8	12.1	12.7	14.3	9.5	1.6	8.6



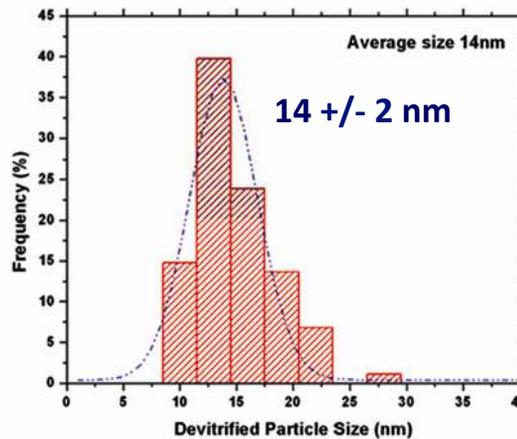
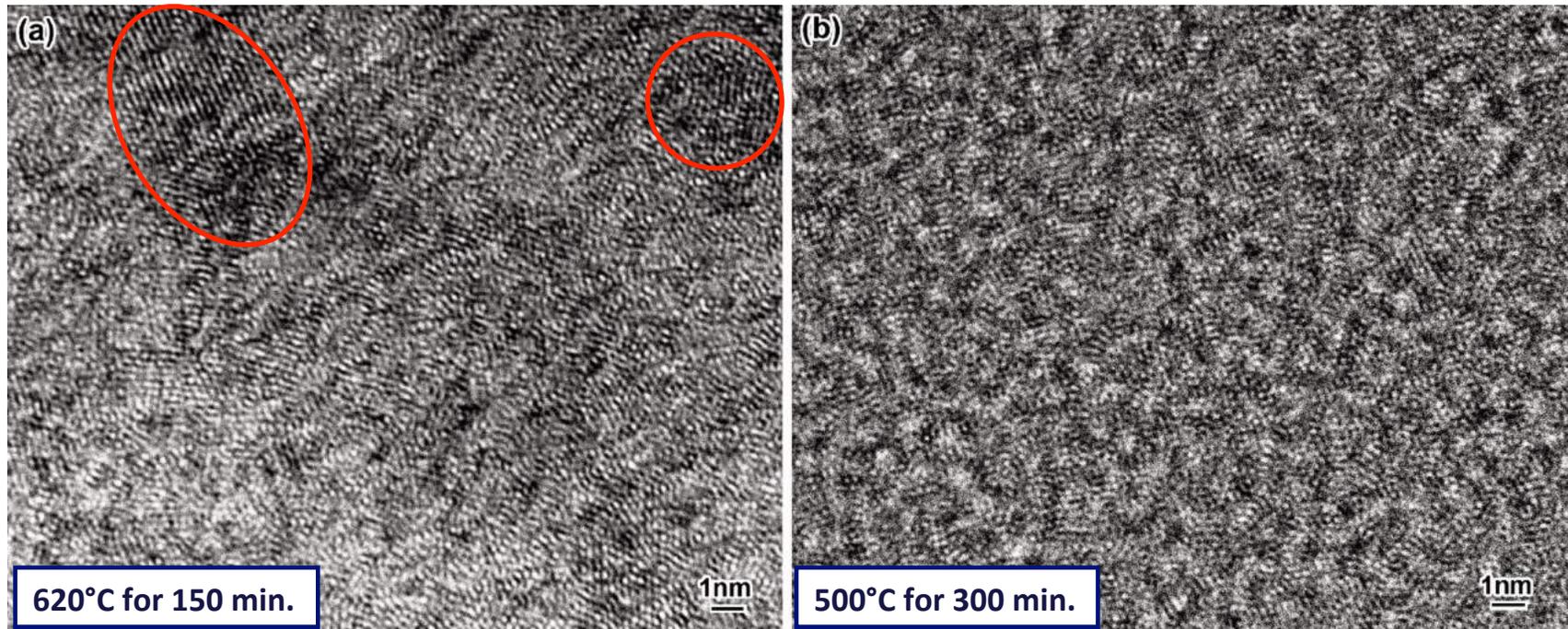
A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

Sequence of Structure Evolution

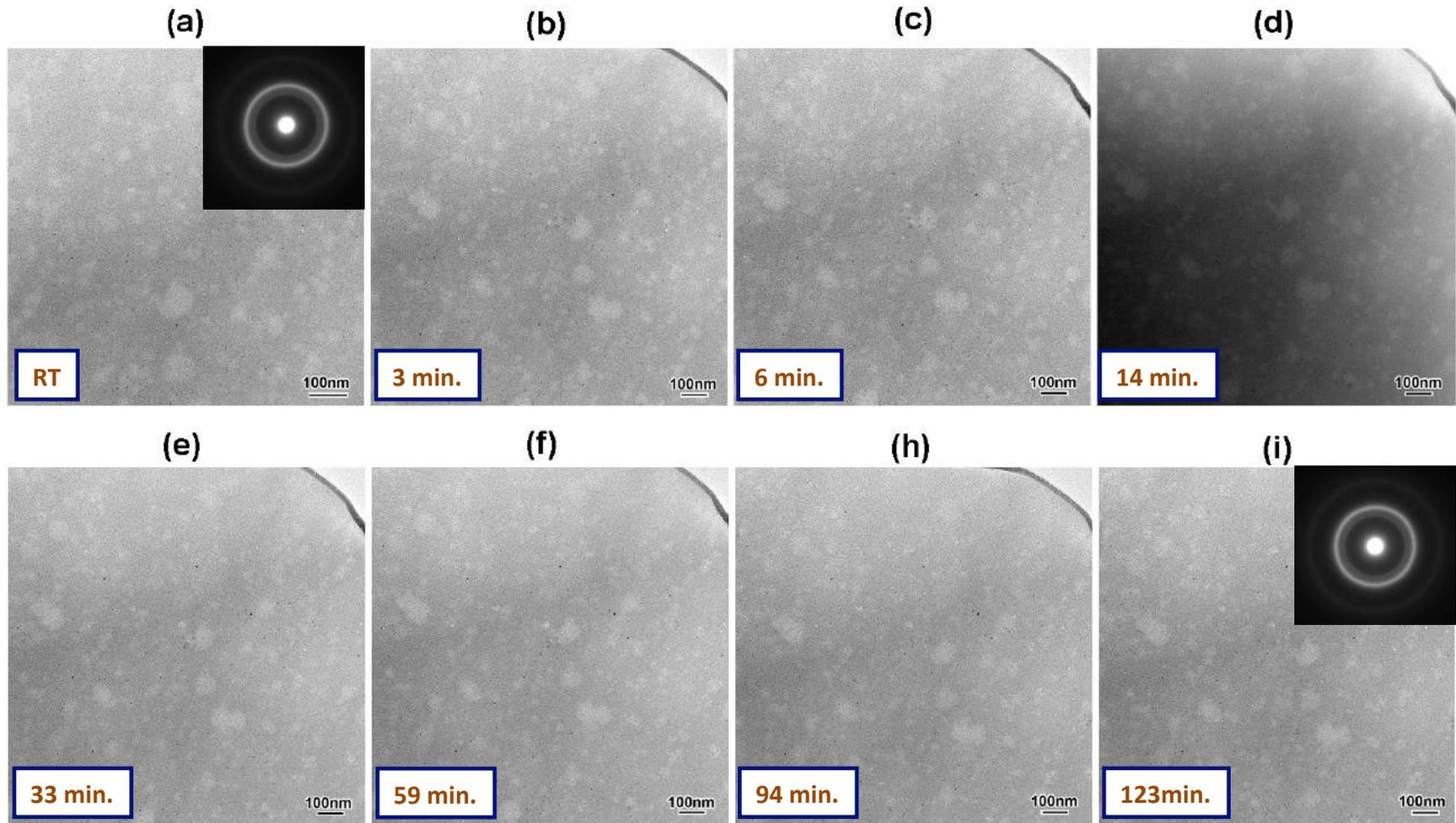


Conventional TEM - HREM



A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

In-situ TEM – Evolution as a Function of Time at 500°C

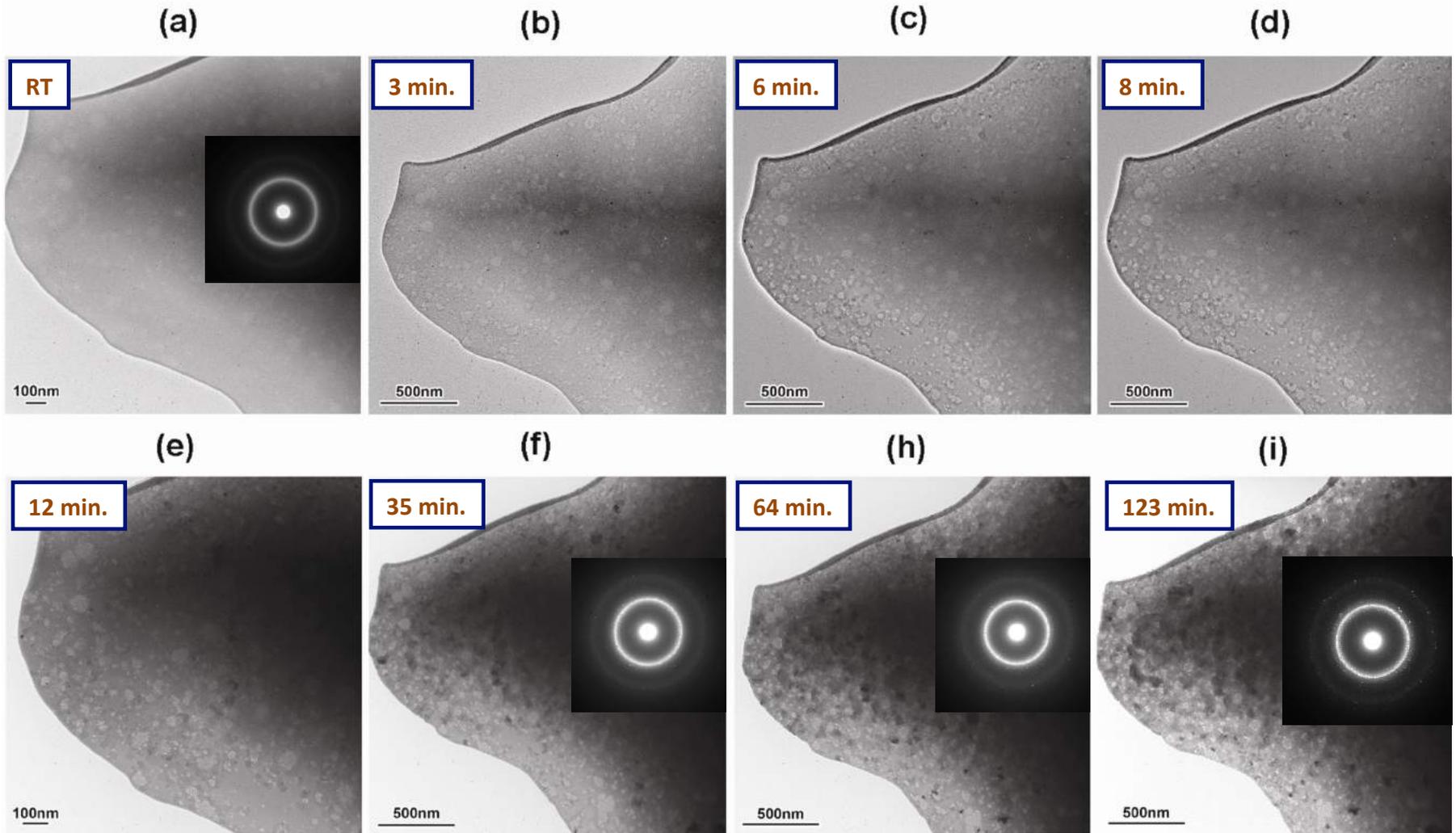


Heating rate: 10 K/min.



A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

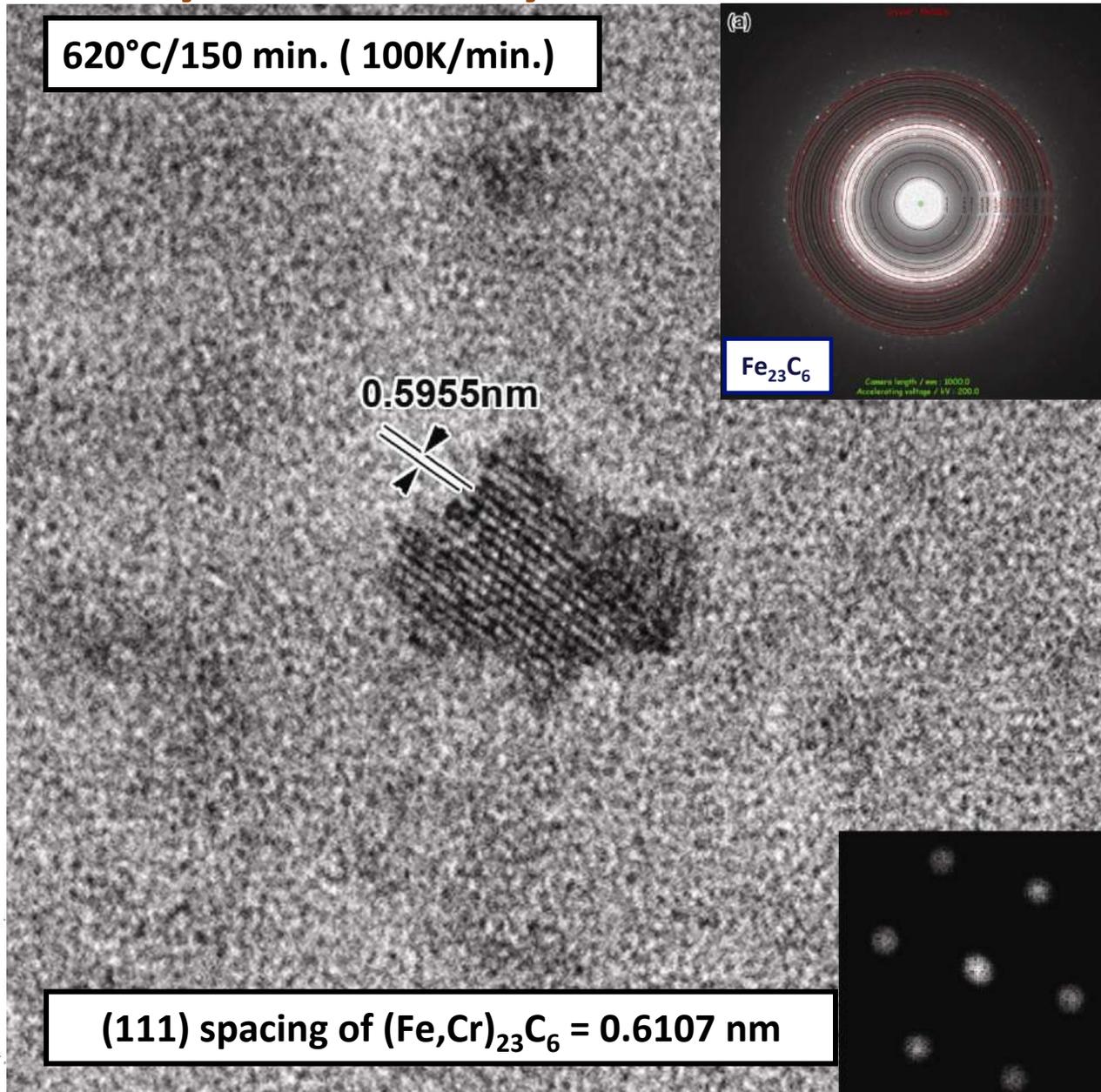
In-situ TEM – Evolution as a Function of Time at 620°C



Heating rate: 10 K/min.

A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

Analysis of the Crystalline Phase



Fe_{23}C_6 :

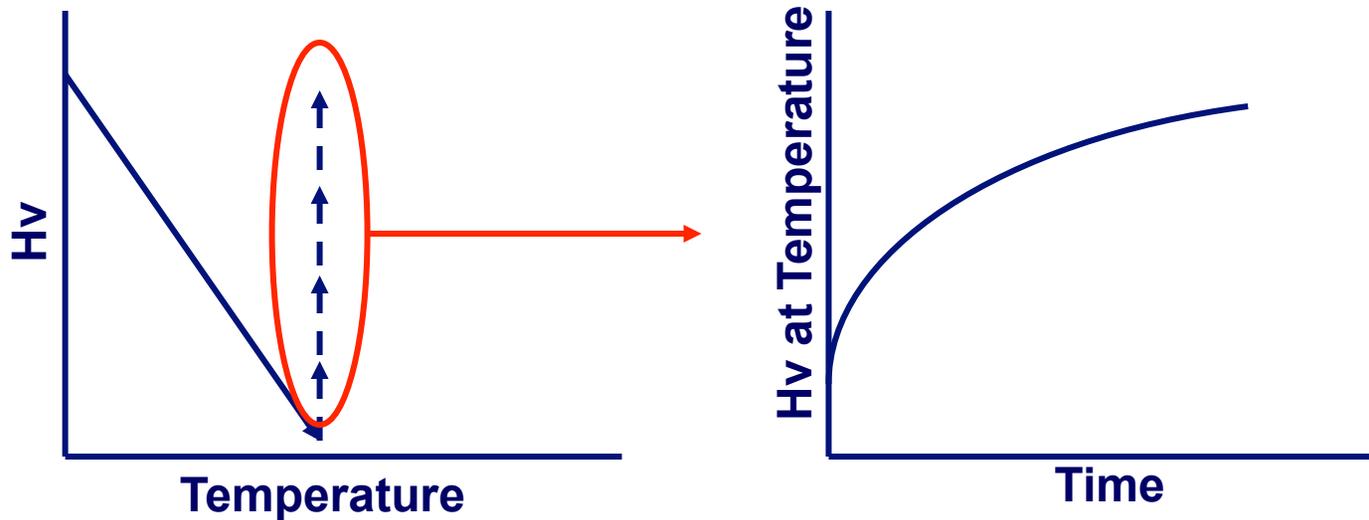
FCC ; $a=1.0578 \text{ nm}$

Fe_7C_3 :

HCP ; $a=0.6882 \text{ nm}, c=0.454 \text{ nm}$

Experimental Procedures: Thermal Exposure Effects

→ Hv Evolution vs. Time at Temperature



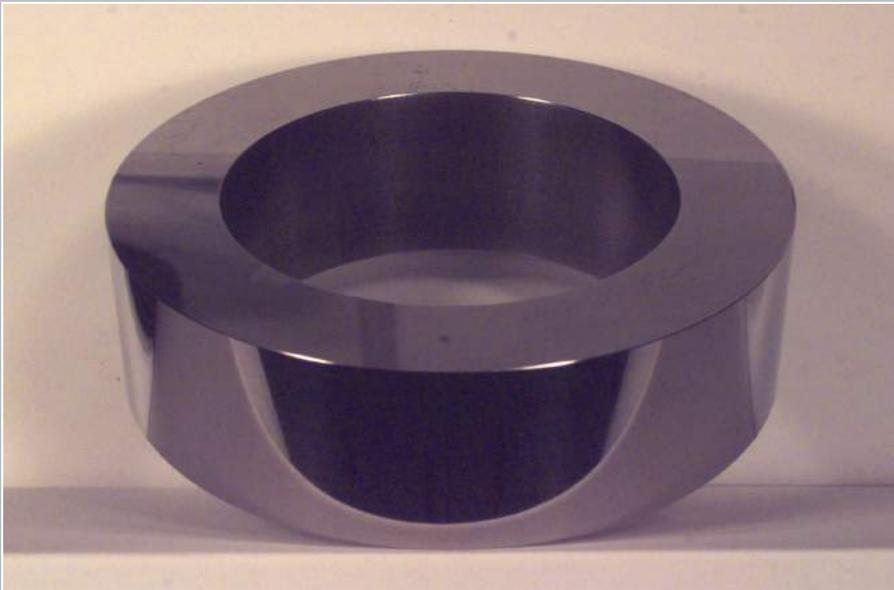
— Temperatures Chosen:

150°C, 275°C, 300°C, 400°C, 500°C, 575°C, 600°C, 620°C



A.S. Nouri, Y. Liu, JJ Lewandowski, Metall. Trans. A, 40A, 1314- 1323 (2009).

Examples of Cylinders w/Fe-Based Metallic Glass Coating



(a) Perspective view of hollow cylinder (shaft) with wear-resistant DAR-type HVOF coating having high-integrity interfacial bond on outer diameter.



(b) Plan view of hollow cylinder (shaft) with wear-resistant DAR-type HVOF coating with high integrity interfacial bond.

Outline

CWRU Activities Connected to Additive/Advanced Manufacturing

- ASTM F42 Definitions
- Example of Desire for Corrosion Resistant and Damage Tolerant Coating
 - Issues of Material Choice (Glass Forming, Damage Tolerant)
 - Thermal Stability, Microstructure Development, Properties
- America Makes/NAMII (National Additive Mfg Innovation Institute)
 - Powder Bed, Directed Energy Deposition (Laser Hot Wire)



Summary

- **Stress State Effects on Flow/Fracture of BMGs at RT ($T \ll T_g$)**
 - **Minimal Effect of Superimposed Pressure on Strength/Plasticity**
- **Stress State and Temperature Effects on BMGs ($T \approx T_g$)**
 - **BIG Effects of Superimposed Pressure on Strength/Plasticity (Strength/Viscosity $\uparrow\uparrow$, Plasticity $\downarrow\downarrow$)**
- **Quasi-Static Fracture Behavior**
 - **Fracture Behavior/Damage Tolerance = $f(\mu/B, v)$**
 - Alloy Design - Fe-based BMG, Ti-based BMG
- **Creation of Micro/Nano Metallic Glass Wires**
 - **Review of Recent Techniques**
 - **Initial Testing of Micro/Nano Wires**
 - **Effects of Sample Size and Preparation on Plasticity**
- **Advanced/Additive Manufacturing**
 - **Metallic Glass Coatings via HVOF**

